# PART I.

## THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN RUBIDIUM AND AMMONIUM SALTS IN TERNARY MIXTURES OF GLYCEROL, ACETONE AND WATER AT 15°, 25°, 35°.

# PART II.

## THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN BINARY AND TERNARY SALTS IN FORMAMID.

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## DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

By

WILLIS S. PUTNAM

June 1915.

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# PART I.

## THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN RUBIDIUM AND AMMONIUM SALTS IN TERNARY MIXTURES OF GLYCEROL, ACETONE AND WATER AT 15°, 25°, 35°.

## INTRODUCTION

In 1901 investigations were begun in this laboratory on the properties of solutions in mixed solvents, and these have been in progress continually to the present.

The solvents that have been studied are water, methyl, and ethyl alcohols, acetone, and glycerol and binary and ternary mixtures of these solvents. The investigations have had to do with freezing point lowering, conductivity and viscosity of typical electrolytes in these solvents. They have established many important points bearing on the nature of solutions, and have brought to light much evidence in support of the solvate theory of solution proposed by Jones. The data obtained has been published in full and thoroughly discussed by Jones and his collaborators in Publications of the Carnegie Institution of Washington Nos. 80 and 180.

The investigations just preceeding the present one were carried out by Jones and Guy, and Jones and Davis, who studied glycerol and glycerol water mixtures, and by Jones, Davis and Hughes, who worked with acetone water mixtures. The present investigation of ternary solvents of glycerol acetone and water is a natural sequence of the recent work mentioned above.

Rubidium and ammonium salts were employed because of their unusual property of causing negative viscosity in several pure and mixed solvents.

The viscosity phases of this investigation have been fully discussed by Davis in Publication No. 210 of the Carnegie Institute of Washington, hence only a brief reference to the work of Jones and his collaborators on viscosity phenomena will be made here.

No satisfactory explanation of negative viscosity had ever been offered until Jones and Veasey[1] studied the problem. Thorpe and Roger[2] had advanced the hypothesis that viscosity was a function of the frictional surfaces of the particles of the liquids. From

1. Carnegie Institute of Washington. Publication No. 80.
2. Zeit. Phys. Chem. 14.361. (1894) 19.323 (1896)

this it follows that frictional surface and viscosity will depend on the size of these particles. Molecular volume is obtained by dividing molecular weight by density. The salts causing negative viscosity have extremely large molecular volume and larger than those constituting the solvent. The introduction of these large particles into the solvent should lower its viscosity.

In all studies of mixed solvents, they have given lower conductivity and fluidity values than the average calculated from the conductivities and fluidities of the components. The Dutoit and Aston hypothesis states that only associated liquids can dissociate molecules. To explain the low conductivity and fluidity values in solvents consisting of two or more assiciated liquids, Jones and Lindsay[3] applied the Dutoit and Aston[4] hypothesis as follows: when two associated liquids are mixed, the association of each is lowered by the presence of the other. The size of the particles is thus reduced and also the fluidity. Conductivity and fluidity curves are similar i. e., conductivity is reduced by the lowered fluidity. The decreased association in the mixed solvents diminishes the dissociation and is therefore another factor in lowering the conductivity. Subsequent workers in this laboratory have obtained a large amount of experimental evidence in support of these hypotheses, and this has been published in the monographs of the Carnegie Institute of Washington to which reference has been made.

Jones, with Bingham,[5] and later with Mahin,[6] worked with mixed solvents of which one component was acetone. In studying the effect of acetone as a constituent of a mixed solvent, four of its important properties must be kept in mind. As a disassociating agent acetone is probably one-fourth that of water. Its fluidity is about 2.5 times that of water, and some salts polymerize in it. It is an associated liquid, having a factor of 1.26 compared with 4.00 for water. Consider Mahin's fluidity curve for acetone and water. For 25 per cent. and 50 per cent. acetone the fluidity is decreased from that of water by the decrease in association. At 75 per cent. and 100 per cent. acetone the fluidity of acetone is the predominating factor.

Consider Mahin's conductivity curve for lithium nitrate in the acetone-water solvent. Mahin shows experimentally that this salt polymerizes in acetone, and it seems clear that this action would be stronger in the more concentrated solutions. The curve shows a sharp downward turn from 75 per cent. to 100 per cent. acetone due probably to polymerization. The two curves are

3. Carnegie Institute of Washington. Publication No. 80.
4. Compt. Rend. 125, 240 (1897)
5. Carnegie Institute of Washington Publication No. 80.
6. Carnegie Institute of Washington Publication No. 180.

parallel to the 75 per cent. point. The N/10000 curve is much like the fluidity curve for the solvent.

Referring to Bingham's curve for potassium iodide in the acetone-water solvent at concentrations from N/200 to N/1600; from 0 per cent. to 50 per cent. it shows effect of decreasing fluidity and dissociation. From 75 per cent. to 100 per cent. the curve turns sharply upward showing the predominating effect of fluidity and that this salt is probably not polymerized at these dilutions. In sharp contrast, Bingham's curve for calcium nitrate in the same solvent turns sharpy down between 75 per cent. and 100 per cent. indicating a strong polymerization action. The lithium nitrate curve in the same solvent is similar. For the concentrated solution, both the calcium and lithium nitrate curves and Hughes' curves for rubidium iodide and bromide show decrease in conductivity from low to high percentages of acetone. Calcium nitrate, a salt which forms solvates and rubidium salts which do not form solvates, give similar curves, which would indicate that solvation is not a factor to be considered here. All influences unite to overcome the fluidity of acetone and produce a curve whose direction is continually downward. If dilute solutions polymerize in pure acetone, it is quite probable that concentrated solutions would do the same in solvents containing 75 per cent. acetone.

Jones and Davis publish curves for ammonium iodide and rubidium bromide in glycerol-water mixtures. The relative fluidity of glycerol and water are 1.0 to 700. These curves turn steadily upward from 100 per cent. glycerol to 100 per cent. water, and indicate that fluidity is the predominating influence.

The foregoing discussion of the curves of Bingham, Mahin, Davis and Hughes does not necessarily represent their views, but was suggested to the writer by the data obtained during the present investigation.

The following data are given here as they have an important bearing on this investigation. The dielectric constants were obtained by Drude[7] and the association factors by Ramsay and Shields.[8]

| Solvent | Dielectric Constant. | Association Factors. |
|---|---|---|
| Water | 81.7 at 18° | 3.81 at 20° |
| Glycerol | 16.5 at 18° | 1.80 at 20° |
| Acetone | 20.7 at 18° | 1.26 at 20° |

**Glycerol and Acetone as Solvents.**

Little work had been done with glycerol as a solvent before Jones and Schmidt began their investigation. Cattaneo[9] had

7. Weid Ann. 60 500.
8. Zeit Phys. Chem, 12,433, (1893)
9. Rend. R, Accad, Lincei[5] 2, 11 112 [1893]

studied the conductivity of some metallic halides and obtained very low values. The viscosity of glycerol-water mixtures was measured by Schöttner.[10] Mixtures of water with several organic solvents were studied by Arrhenius,[11] and it was found that large viscosity values gave large temperature coefficients. Schall and Van Ryn[12] investigated the relative viscosities of glycerol-water and glycerol-alcohol mixtures. Lemke[13] measured the conductivity and viscosity of glycerol-water mixtures at 25°, and concluded that conductivity was governed both by the viscosity and association of the solvent. The first work done in this laboratory was that of Jones and Schmidt. Their work showed that glycerol is a good solvent for inorganic salts, and a good dissociating agent, as would be expected from its dielectric constant and association factor. They showed that potassium iodide lowered the viscosity of water and a binary solvent containing 25 per cent. and 50 per cent. glycerol. The effects of the salts on the viscosity of the solution is inversely proportional to the atomic volumes of the cations, as was shown by Jones and Veazey for aqueous solutions.

Jones and Guy[14] continued the investigation using a wider range of electrolytes; and as solvents, binary mixtures of glycerol with ethyl and methyl alcohols and with water. Their data show that molecular conductivity values are very low in glycerol, but increase uniformly with increasing dilutions and rise in temperature. Temperature coefficients are extremely large, and salts of barium, strontium, calcium and cobalt which form hydrates in aqueous solutions, have larger temperature coefficients than the salts of ammonium and the alkali metals which show little or no evidence of hydration. Here is good evidence of solvation in glycerol. In the mixed solvents, they found the fluidities and conductivities lower than those calculated from averages. They explained these facts by the hypothesis of Jones and Lindsay.[15] Conductivity and fluidity curves have very nearly the same character.

They found that N/10 solutions in pure glycerol of sodium nitrate, ammonium bromide, ammonium iodide and rubidium bromide produce a large decrease in viscosity. The hypothesis of Jones and Veazey[15] explain these unusual phenomena.

The same line of investigation was continued by Jones and Davis[14] as already stated. They measured the conductivity of ammonium iodide; and the chloride, bromide, iodide, and nitrate

10. Wien. Ber. 682 [1878] 11. Zeit. Phys. Chem. 1 285 [1887]
12. Zeit. Phys. Chem. 23, 329 [1897] 13. Zeit. Phys. Chem. 52, 479 [1905]
14. Carnegie Institute of Washington, Publication No. 180.
15. Carnegie Institute of Washington, Publication No. 80.

of rubidium in pure glycerol at ten degree intervals from 25° to 75°, and also the viscosity of the same solutions from normal to tenth-normal. They also obtained data for molecular conductivities at 25°, 35° and 45° of ammonium iodide and ribidium bromide in mixtures of glycerol and water, and also the viscosity of the same solutions in concentrations from normal to tenth-normal.

Besides confirming many of the conclusions of earlier workers, Davis' investigation established several important points. Most of them were in relation to viscosity. Solutions which had a viscosity much below that of the solvent gave minima in the conductivity curves for concentrations normal to tenth-normal. The conductivity varied directly with the fluidity. Rubidium salts lower the viscosity of glycerol more than potassum salts. Ammonium salts act more like salts of rubidium that like potassum salts. Rubidium salts do not produce positive viscosity in glycerol even at 75°.

Nearly all that is known of acetone in relation to conductivity and viscosity is from the work in this laboratory. It is a poor solvent for inorganic salts, and has been studied chiefly in mixtures with water and ethyl and methyl alcohols. The work of some of the earlier investigators has already been discussed. The studies previously mentioned of Jones, Davis and Hughes have a direct bearing on the present investigation. They measured the conductivity and viscosity in acetone-water mixtures of the same rubidium salts that were used in the glycerol-water work, using the same concentrations, and at temperatures from 15° to 45°. As in all mixed solvents, values for conductivity and fluidity were less than those calculated from averages. These salts decrease viscosity only in solvents containing 50 per cent. or less of acetone. Negative viscosity coefficients were much less than for water or glycerol. There is some evidence of solvation of rubidium salts in dilute solutions.

# EXPERIMENTAL

### Apparatus.

The constant temperature baths used for this investigation were like those previously employed for such work in this laboratory. A cooling coil was used in each bath and constant water pressure was maintained by a standpipe. By means of thermostats and an electrically controlled gas regulator designed by Reid,[16] the temperature was maintained constant to within 0.02°. Beckmann thermometers which were graduated to 0.05° were used in the

16. Amer. Chem. Jour. 41, 148 (1909)

baths. Frequent comparisons were made with a thermometer standardized by the Bureau of Standards of Washington, D. C.

The conductivity measurements were made by the usual Kohlrausch method. The slide wire Wheatstone bridge, having a wire five meters in length was made and standardized by Leeds & Northrop of Philadelphia, Pa. The resistances were compared with a rheostat that had been standardized by the Bureau of Standards of Washington. An alternating current was obtained by use of an induction coil, and the minimum point was detected by a telephone receiver. A double system of wiring was used between the resistance, bridge and cells. By means of a double switch, the arms of the bridge could be interchanged. Both sides were read which gave duplicate readings. The circuit was opened and closed by a telegraph key. All copper wire used in the circuit was No. 12 gauge which had a negligible resistance for the length in use. All connections were soldered. The resistances used were from 20 to 3000 ohms. Bridge readings **a** and **b** agreed to within one millimeter and usually much closer.

Three types of cells were used. N/2 solutions were measured in a U cell having a constant of about 15000. The solvents were measured in cylinder cells described by Jones and Schmidt[17] and Jones and Kreider[18] having constants from 2.05 to 4.46. For solutions from N/4 to N/800 the usual plate cells described by Jones and Bingham were used having constants from 11 to 338.

Measuring flasks and pipettes were calibrated by direct weighing to hold aliquot parts of a liter at 20°.

Glycerol, acetone and water as solvents were measured in 100 c. c. and 200 c. c. pipettes. The amount of glycerol they would deliver in a given time at 20° was weighed and the amount necessary to make 100 c. c. or 200 c. c. was added from a graduated pipette.

## Solvents.

**Water.** The water was purified by the method of Jones and Mackay[19] as modified by Schmidt,[20] and had a mean specific conductivity of $1.5 \times 10^{-6}$ at 25°.

**Acetone.** The pure acetone of Kahlbaum was allowed to stand several days over calcium chloride and distilled. The mixed solvent and solutions were made as soon as possible after the distil-

17, Carnegie Institute of Washington Publication No, 180.
18, Carnegie Institute of Washington Publication No. 80
19, Amer, Chem, J. 17. 83 [1895]
20, Loc, Cit,

lation of the acetone. The conductivity was about the same as that of the water purified as described above.

**Glycerol.** The glycerol used was Kahlbaum's "Doppelt-Dist. 1.26" having a specific conductivity of 0.6 x $10^{-7}$ at 25°. Redistillation was omitted as Schmidt has shown that it does not appreciably decrease its conductivity or increase its purity.

**The Mixed Solvents.** Glycerol and acetone are only slightly miscible. To a flask containing two parts each of glycerol and acetone it was found necessary to add one part of water to obtain a homogeneous mixture. This method gave the 2-2-1 solvent. An N/2 solution of ammonium bromide in this solvent could not be made, since the acetone was salted out, showing how near the limit of miscibility was reached in the pure solvent.

### Solutions.

All solutions were made at 20°. N/2, N/4 and N/10 solutions were made by direct weighing of the anhydrous salt which had been dried for an hour or more at 120° to 130°. The N/50 and N/200 solutions were made by diluting the N/10, and the N/800 was made by dilution from the N/50. Jena Normal flasks and pipettes were used to remove, as far as possible, the chance of action on the glass by the solvent.

### Salts.

The salts of rubidium and ammonium that were used were the best that could be obtained from Kahlbaum. They were recrystalized from conductivity water and thoroughly dried, before weighing, at 120° to 130°. The ammonium iodide was pure white after drying and the solutions were colorless at the time the measurements were made.

# PROCEDURE

### Conductivity Measurements.

The values of molecular conductivity were calculated from the formula $\mathrm{M}v = \frac{\mathrm{K}va}{\mathrm{Wb}}$ K is the cell constant, $v$ is the number of liters containing a gram-molecule of the salt, W is the resistance in ohms, a and b are the Wheatstone bridge readings.

A N/50 potassium chloride solution in water was the basis for determining cell constants. Its conductivity was taken as 129.7 reciprocal Siemens units at 25°, as given by Ostwald. Three resistances were used in measuring each solution, and they were so chosen as to keep the bridge readings between 400 and 600. A slight error was unavoidable on account of the variation in the cell constants. They were however checked at frequent intervals during the investigation. It is probable that the error for molecular conductivity never exceeds 1.0 per cent.

### Temperature Coefficients.

Temperature coefficients in conductivity units are the increase in conductivity for each degree of rise in temperature. The temperatures compared always differ by 10°. The formula is therefore

$$\text{Temp. coef.} = \frac{\mathrm{M}v \text{ at } t' - \mathrm{M}v \text{ at } t''}{10}$$

The above, divided by the conductivity at the lower temperature gives the per cent. coefficient.

# MEASUREMENTS

## TABLE I.

**Specific Conductivity of Solvents at 15°-25°-35°.**

| | 15° | 25° | 35° |
|---|---|---|---|
| 1-1-1 | .00237 | .00332 | .00453 |
| 1-2-1 | .00215 | .00294 | .00390 |
| 1-1-2 | .00368 | .00508 | .00676 |
| 1-2-2 | .00343 | .00468 | .00613 |
| 2-1-1 | .00132 | .00202 | .00293 |
| 2-1-2 | .00233 | .00333 | .00458 |
| 2-2-1 | .00139 | .00202 | .00283 |

In naming the solvents, the following order is always followed: Glycerol - Acetone - Water. Thus the 1-2-1 solvent means that it consists of one part glycerol, two parts acetone and one part water.

## TABLE II.

**Molecular Conductivity of Ammonium Iodide in the 1-1-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 15.57 | 20.51 | 25.87 |
| 4 | 16.86 | 23.04 | 30.35 |
| 10 | 17.43 | 23.68 | 31.84 |
| 50 | 17.87 | 24.38 | 33.20 |
| 200 | 18.72 | 26.05 | 34.67 |

## TABLE III.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0317 | 0.0261 | 0.494 | 0.536 |
| 4 | 0.0366 | 0.0317 | 0.618 | 0.731 |
| 10 | 0.0359 | 0.0345 | 0.625 | 0.816 |
| 50 | 0.0364 | 0.0362 | 0.651 | 0.882 |
| 200 | 0.0392 | 0.0331 | 0.733 | 0.862 |

## TABLE IV.

### Molecular Conductivity of Rubidium Iodide in the 1-1-1 Solvent at 15°-25°-35°.

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 16.07 | 21.95 | 28.81 |
| 4 | 16.67 | 22.93 | 29.98 |
| 10 | 17.65 | 24.24 | 31.90 |
| 50 | ..... | ..... | ..... |
| 200 | 19.23 | 26.73 | 34.09 |

## TABLE V.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0366 | 0.0313 | 0.588 | 0.686 |
| 4 | 0.0375 | 0.0307 | 0.626 | 0.705 |
| 10 | 0.0373 | 0.0316 | 0.659 | 0.766 |
| 50 | ..... | ..... | ..... | ..... |
| 200 | 0.0389 | 0.0275 | 0.750 | 0.736 |

## TABLE VI.

**Molecular Conductivity of Ammonium Bromide in the 1-1-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 15.21 | 20.57 | 27.11 |
| 4 | 15.71 | 21.41 | 28.45 |
| 10 | 16.56 | 22.58 | 30.03 |
| 50 | 17.84 | 24.59 | 32.88 |
| 200 | 18.50 | 25.52 | 34.13 |

## TABLE VII.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0352 | 0.0318 | 0.536 | 0.654 |
| 4 | 0.0363 | 0.0329 | 0.570 | 0.704 |
| 10 | 0.0363 | 0.0326 | 0.602 | 0.745 |
| 50 | 0.0378 | 0.0337 | 0.675 | 0.829 |
| 200 | 0.0379 | 0.0338 | 0.702 | 0.863 |

## TABLE VIII.

**Molecular Conductivity of Rubidium Bromide in the 1-1-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 15.22 | 20.56 | 26.80 |
| 4 | 15.68 | 21.20 | 28.02 |
| 10 | 16.51 | 22.53 | 29.71 |
| 50 | 17.67 | 24.41 | 32.35 |
| 200 | 18.19 | 25.30 | 33.43 |

## TABLE IX.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0351 | 0.0304 | 0.534 | 0.624 |
| 4 | 0.0352 | 0.0332 | 0.552 | 0.682 |
| 10 | 0.0365 | 0.0319 | 0.602 | 0.718 |
| 50 | 0.0381 | 0.0325 | 0.674 | 0.794 |
| 200 | 0.0381 | 0.0321 | 0.711 | 0.813 |

## TABLE X.

**Molecular Conductivity of Ammonium Iodide in the 1-2-1 Solvent 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 18.23 | 23.66 | 30.28 |
| 4 | 18.80 | 24.67 | 31.26 |
| 10 | 19.88 | 26.36 | 33.54 |

## TABLE XI.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0298 | 0.0283 | 0.543 | 0.662 |
| 4 | 0.0312 | 0.0267 | 0.587 | 0.659 |
| 10 | 0.0326 | 0.0272 | 0.648 | 0.718 |

## TABLE XII.

**Molecular Conductivity of Rubidium Iodide in the 1-2-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 18.33 | 23.81 | 30.24 |
| 4 | 19.00 | 24.68 | 31.41 |
| 10 | 20.00 | 28.28 | 33.74 |
| 50 | 21.40 | 26.22 | 36.51 |
| 200 | 22.56 | 29.58 | 38.69 |
| 800 | 24.23 | 32.80 | 42.00 |

## TABLE XIII.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0299 | 0.0270 | 0.548 | 0.643 |
| 4 | 0.0299 | 0.0273 | 0.568 | 0.673 |
| 10 | 0.0311 | 0.0287 | 0.622 | 0.752 |
| 50 | 0.0322 | 0.0291 | 0.688 | 0.823 |
| 200 | 0.0323 | 0.0296 | 0.729 | 0.884 |
| 800 | 0.0354 | 0.0280 | 0.857 | 0.920 |

## TABLE XIV.

**Molecular Conductivity of Ammonium Bromide in the 1-2-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 15.04 | 19.72 | 24.94 |
| 4 | 15.41 | 20.45 | 26.24 |
| 10 | 17.34 | 22.81 | 29.23 |
| 50 | 19.28 | 25.82 | 33.22 |

## TABLE XV.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0311 | 0.0265 | 0.468 | 0.522 |
| 4 | 0.0327 | 0.0283 | 0.504 | 0.579 |
| 10 | 0.0315 | 0.0282 | 0.547 | 0.642 |
| 50 | 0.0339 | 0.0287 | 0.654 | 0.740 |

## TABLE XVI.

### Molecular Conductivity of Rubidium Bromide in the 1-2-1 Solvent at 15°-25°-35°.

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 14.78 | 19.35 | 24.49 |
| 4 | 15.82 | 20.74 | 26.45 |
| 10 | 17.24 | 22.69 | 29.12 |
| 50 | 19.10 | 25.50 | 32.87 |

## TABLE XVII.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0309 | 0.0266 | 0.457 | 0.514 |
| 4 | 0.0311 | 0.0275 | 0.492 | 0.571 |
| 10 | 0.0316 | 0.0283 | 0.545 | 0.643 |
| 50 | 0.0335 | 0.0289 | 0.640 | 0.737 |

## TABLE XVIII.

**Molecular Conductivity of Ammonium Iodide in the 1-1-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 27.54 | 35.86 | 46.36 |
| 4 | 26.40 | 35.22 | 45.21 |
| 10 | 27.93 | 37.62 | 48.68 |
| 50 | 28.88 | 38.97 | 50.67 |
| 200 | 30.82 | 41.47 | 54.02 |
| 800 | 31.86 | 43.01 | 56.34 |

## TABLE XIX.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0302 | 0.0293 | 0.832 | 1.050 |
| 4 | 0.0334 | 0.0284 | 0.882 | 0.999 |
| 10 | 0.0347 | 0.0294 | 0.969 | 1.106 |
| 50 | 0.0347 | 0.0300 | 1.001 | 1.170 |
| 200 | 0.0346 | 0.0303 | 1.065 | 1.255 |
| 800 | 0.0350 | 0.0310 | 1.115 | 1.333 |

## TABLE XX.

**Molecular Conductivity of Rubidium Iodide in the 1-1-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 27.42 | 35.96 | 45.94 |
| 4 | 26.80 | 35.39 | 45.36 |
| 10 | 28.17 | 37.52 | 48.67 |
| 50 | 29.17 | 38.98 | 51.16 |
| 800 | 32.40 | 43.92 | 57.46 |

## TABLE XXI

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0311 | 0.0278 | 0.854 | 0.998 |
| 4 | 0.0320 | 0.0282 | 0.859 | 0.997 |
| 10 | 0.0332 | 0.0297 | 0.935 | 1.115 |
| 50 | 0.0336 | 0.0312 | 0.981 | 1.218 |
| 800 | 0.0356 | 0.0308 | 1.152 | 1.354 |

## TABLE XXII.

### Molecular Conductivity of Ammonium Bromide in the 1-1-2 Solvent at 15°-25°-35°.

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 26.57 | 35.19 | 44.71 |
| 4 | 25.98 | 34.29 | 43.03 |
| 10 | 27.85 | 37.20 | 47.92 |
| 50 | 29.40 | 39.48 | 51.17 |
| 800 | 31.99 | 43.36 | 55.44 |

## TABLE XXIII.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0324 | 0.0263 | 0.862 | 0.952 |
| 4 | 0.0320 | 0.0255 | 0.831 | 0.874 |
| 10 | 0.0336 | 0.0288 | 0.935 | 1.072 |
| 50 | 0.0343 | 0.0296 | 1.008 | 1.169 |
| 800 | 0.0349 | 0.0279 | 1.117 | 1.208 |

## TABLE XXIV.

**Molecular Conductivity of Rubidium Bromide in the 1-1-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 26.35 | 34.62 | 44.31 |
| 4 | 25.59 | 33.45 | 41.99 |
| 10 | 28.02 | 37.23 | 48.03 |
| 50 | 28.75 | 39.86 | 51.71 |

## TABLE XXV.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0314 | 0.0280 | 0.827 | 0.969 |
| 4 | 0.0307 | 0.0255 | 0.786 | 0.845 |
| 10 | 0.0329 | 0.0290 | 0.921 | 1.080 |
| 50 | 0.0386 | 0.0297 | 1.111 | 1.185 |

## TABLE XXVI.

**Molecular Conductivity of the Ammonium Iodide in the 1-2-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 25.81 | 33.87 | 42.86 |
| 4 | 26.60 | 34.99 | 44.44 |
| 10 | 28.72 | 38.00 | 48.70 |
| 50 | 29.94 | 39.78 | 50.73 |
| 200 | 31.14 | 41.69 | 53.60 |

## TABLE XXVII.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0312 | 0.0265 | 0.806 | 0.899 |
| 4 | 0.0315 | 0.0270 | 0.839 | 0.945 |
| 10 | 0.0323 | 0.0282 | 0.928 | 1.070 |
| 50 | 0.0329 | 0.0275 | 0.984 | 1.095 |
| 200 | 0.0339 | 0.0286 | 1.055 | 1.191 |

## TABLE XXVIII.

### Molecular Conductivity of Rubidium Iodide in the 1-2-2 Solvent at 15°-25°-35°.

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 25.90 | 33.99 | 42.76 |
| 4 | 25.74 | 33.58 | 43.85 |
| 10 | 27.03 | 36.75 | ..... |
| 50 | 30.08 | 40.08 | 51.10 |
| 200 | 30.61 | 41.00 | 52.49 |

## TABLE XXIX.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0312 | 0.0258 | 0.809 | 0.877 |
| 4 | 0.0305 | 0.0306 | 0.784 | 1.027 |
| 10 | 0.0360 | ..... | 0.972 | ..... |
| 50 | 0.0332 | 0.0275 | 1.000 | 1.102 |
| 200 | 0.0339 | 0.0280 | 1.039 | 1.149 |

## TABLE XXX.

**Molecular Conductivity of Ammonium Bromide in the 1-2-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 24.16 | 31.57 | 39.59 |
| 4 | 23.89 | 31.15 | 39.43 |
| 10 | 25.65 | 33.55 | 42.34 |
| 50 | ..... | 38.41 | 49.18 |
| 200 | 30.72 | 40.93 | 52.31 |

## TABLE XXXI.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0308 | 0.0254 | 0.741 | 0.802 |
| 4 | 0.0304 | 0.0266 | 0.726 | 0.828 |
| 10 | 0.0308 | 0.0262 | 0.790 | 0.879 |
| 50 | ..... | 0.0280 | ..... | 1.077 |
| 200 | 0.0332 | 0.0278 | 1.021 | 1.138 |

## TABLE XXXII.

**Molecular Conductivity of Rubidium Bromide in the 1-2-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 23.50 | 30.93 | 39.20 |
| 4 | 23.14 | 29.33 | 35.92 |
| 10 | 25.87 | 32.06 | 39.39 |
| 50 | 29.10 | 37.09 | 47.57 |
| 200 | 30.60 | 39.84 | 50.55 |

## TABLE XXXIII.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0316 | 0.0267 | 0.743 | 0.827 |
| 4 | 0.0267 | 0.0225 | 0.619 | 0.659 |
| 10 | 0.0239 | 0.0242 | 0.619 | 0.733 |
| 50 | 0.0275 | 0.0283 | 0.799 | 1.048 |
| 200 | 0.0302 | 0.0269 | 0.924 | 1.071 |

## TABLE XXXIV.

**Molecular Conductivity of Ammonium Iodide in the 2-1-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 8.08 | 11.79 | 16.46 |
| 4 | 8.16 | 11.97 | 16.77 |
| 10 | 8.38 | 12.29 | 17.31 |
| 50 | 8.87 | 13.10 | 18.55 |
| 800 | 8.69 | 12.84 | 18.36 |

## TABLE XXXV.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0459 | 0.0396 | 0.371 | 0.467 |
| 4 | 0.0467 | 0.0401 | 0.381 | 0.480 |
| 10 | 0.0467 | 0.0408 | 0.391 | 0.502 |
| 50 | 0.0477 | 0.0416 | 0.423 | 0.545 |
| 800 | 0.0478 | 0.0430 | 0.415 | 0.552 |

## TABLE XXXVI

**Molecular Conductivity of Rubidium Iodide in the 2-1-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 7.92 | 11.31 | 16.18 |
| 4 | 8.02 | 11.79 | 16.52 |
| 10 | 8.26 | 12.16 | 17.10 |
| 50 | 8.53 | 12.67 | 17.93 |
| 800 | 9.26 | 13.99 | 20.01 |

## TABLE XXXVII.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0420 | 0.0433 | 0.333 | 0.487 |
| 4 | 0.0470 | 0.0401 | 0.377 | 0.473 |
| 10 | 0.0472 | 0.0406 | 0.390 | 0.494 |
| 50 | 0.0485 | 0.0415 | 0.414 | 0.526 |
| 800 | 0.0511 | 0.0430 | 0.473 | 0.602 |

## TABLE XXXVIII.

**Molecular Conductivity of Ammonium Bromide in the 2-1-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 7.91 | 11.20 | 15.82 |
| 4 | 7.83 | 11.25 | 15.61 |
| 10 | 8.23 | 12.06 | 16.88 |
| 50 | 8.56 | 12.67 | 17.80 |
| 800 | 9.19 | 13.55 | 19.34 |

## TABLE XXXIX.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0416 | 0.0413 | 0.329 | 0.462 |
| 4 | 0.0437 | 0.0388 | 0.342 | 0.436 |
| 10 | 0.0465 | 0.0400 | 0.383 | 0.482 |
| 50 | 0.0480 | 0.0405 | 0.411 | 0.513 |
| 800 | 0.0474 | 0.0427 | 0.436 | 0.579 |

## TABLE XL.

### Molecular Conductivity of Rubidium Bromide in the 2-1-1 Solvent at 15°-25°-35°.

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 7.62 | 11.19 | 15.53 |
| 4 | 7.68 | 11.16 | 15.57 |
| 10 | 8.10 | 11.93 | 16.74 |
| 50 | 8.50 | 12.55 | 17.72 |
| 800 | .... | 12.62 | 17.83 |

## TABLE XLI.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0469 | 0.0388 | 0.357 | 0.434 |
| 4 | 0.0453 | 0.0395 | 0.348 | 0.441 |
| 10 | 0.0473 | 0.0403 | 0.383 | 0.481 |
| 50 | 0.0476 | 0.0412 | 0.405 | 0.517 |
| 800 | ..... | 0.0413 | ..... | 0.521 |

## TABLE XLII.

**Molecular Conductivity of Ammonium Iodide in the 2-1-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 15.58 | 21.71 | 28.79 |
| 4 | 15.80 | 22.05 | 29.39 |
| 10 | 16.48 | 22.61 | 30.13 |
| 50 | 17.11 | 24.46 | 32.88 |
| 200 | 17.34 | 24.57 | 33.16 |

## TABLE XLIII.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0393 | 0.0326 | 0.613 | 0.708 |
| 4 | 0.0396 | 0.0333 | 0.625 | 0.734 |
| 10 | 0.0372 | 0.0333 | 0.613 | 0.752 |
| 50 | 0.0430 | 0.0344 | 0.735 | 0.842 |
| 200 | 0.0417 | 0.0350 | 0.723 | 0.859 |

## TABLE XLIV.

**Molecular Conductivity of Rubidium Iodide in the 2-1-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 15.32 | 21.29 | 28.25 |
| 4 | 15.57 | 21.78 | 29.02 |
| 10 | 16.42 | 22.98 | 30.58 |
| 50 | 17.07 | 24.06 | 32.38 |
| 200 | 17.12 | 24.24 | 32.66 |

## TABLE XLV.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0390 | 0.0328 | 0.597 | 0.699 |
| 4 | 0.0399 | 0.0332 | 0.621 | 0.724 |
| 10 | 0.0399 | 0.0331 | 0.656 | 0.760 |
| 50 | 0.0409 | 0.0346 | 0.699 | 0.832 |
| 200 | 0.0416 | 0.0347 | 0.712 | 0.842 |

## TABLE XLVI.

### Molecular Conductivity of Ammonium Bromide in the 2-1-2 Solvent at 15°-25°-35°.

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 15.55 | 21.59 | 28.55 |
| 4 | 15.60 | 21.52 | 28.86 |
| 10 | 16.16 | 22.52 | 30.13 |
| 50 | 16.92 | 23.78 | 32.08 |
| 200 | 17.59 | 24.73 | 33.25 |

## TABLE XLVII.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0388 | 0.0322 | 0.604 | 0.696 |
| 4 | 0.0379 | 0.0341 | 0.592 | 0.734 |
| 10 | 0.0394 | 0.0338 | 0.636 | 0.761 |
| 50 | 0.0406 | 0.0349 | 0.686 | 0.830 |
| 200 | 0.0406 | 0.0345 | 0.714 | 0.852 |

## TABLE XLVIII.

**Molecular Conductivity of Rubidium Bromide in the 2-1-2 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 15.04 | 20.75 | 27.45 |
| 4 | 15.55 | 21.59 | 28.66 |
| 10 | 16.66 | 22.99 | 30.30 |
| 50 | 17.54 | 24.58 | 32.92 |
| 200 | 18.15 | 25.54 | 34.47 |

## TABLE XLIX.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0380 | 0.0323 | 0.571 | 0.670 |
| 4 | 0.0388 | 0.0327 | 0.604 | 0.707 |
| 10 | 0.0380 | 0.0318 | 0.633 | 0.731 |
| 50 | 0.0401 | 0.0339 | 0.704 | 0.834 |
| 200 | 0.0407 | 0.0350 | 0.739 | 0.893 |

## TABLE L.

**Molecular Conductivity of Ammonium Iodide in the 2-2-1 Solvent at 15°-25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | 9.87 | 13.23 | 16.95 |
| 4 | 10.63 | 14.75 | 19.68 |
| 10 | 11.40 | 15.80 | 21.11 |
| 50 | 12.18 | 16.97 | 23.12 |
| 200 | 12.40 | 17.50 | 23.69 |

## TABLE LI.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0340 | 0.0281 | 0.336 | 0.372 |
| 4 | 0.0388 | 0.0334 | 0.412 | 0.493 |
| 10 | 0.0386 | 0.0336 | 0.440 | 0.531 |
| 50 | 0.0393 | 0.0362 | 0.479 | 0.615 |
| 200 | 0.0411 | 0.0354 | 0.510 | 0.619 |

## TABLE LII.

**Molecular Conductivity of Ammonium Bromide in the 2-2-1 Solvent at 15 -25°-35°.**

| V. | 15° | 25° | 35° |
|---|---|---|---|
| 2 | .... | ..... | ..... |
| 4 | 9.09 | 12.44 | 16.85 |
| 10 | 9.81 | 13.71 | 18.42 |
| 50 | 10.62 | 14.99 | 20.43 |
| 200 | 11.21 | 15.93 | 21.77 |

## TABLE LIII.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | ..... | ..... | ..... | ..... |
| 4 | 0.0369 | 0.0355 | 0.335 | 0.441 |
| 10 | 0.0399 | 0.0344 | 0.391 | 0.471 |
| 50 | 0.0411 | 0.0363 | 0.437 | 0.544 |
| 200 | 0.0421 | 0.0367 | 0.472 | 0.584 |

**Note.**—A homogeneous half-normal solution could not be made. The Ammonium Bromide salted out the acetone.

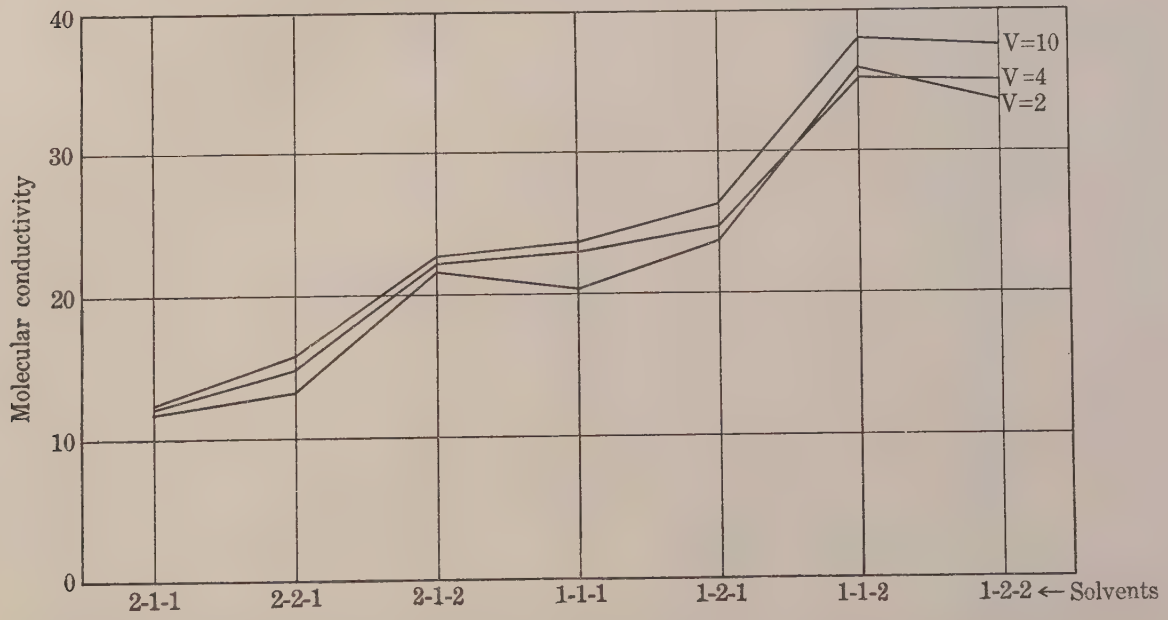


Figure 1.—Conductivity of ammonium iodide in glycerol, acetone, and water at 25°.

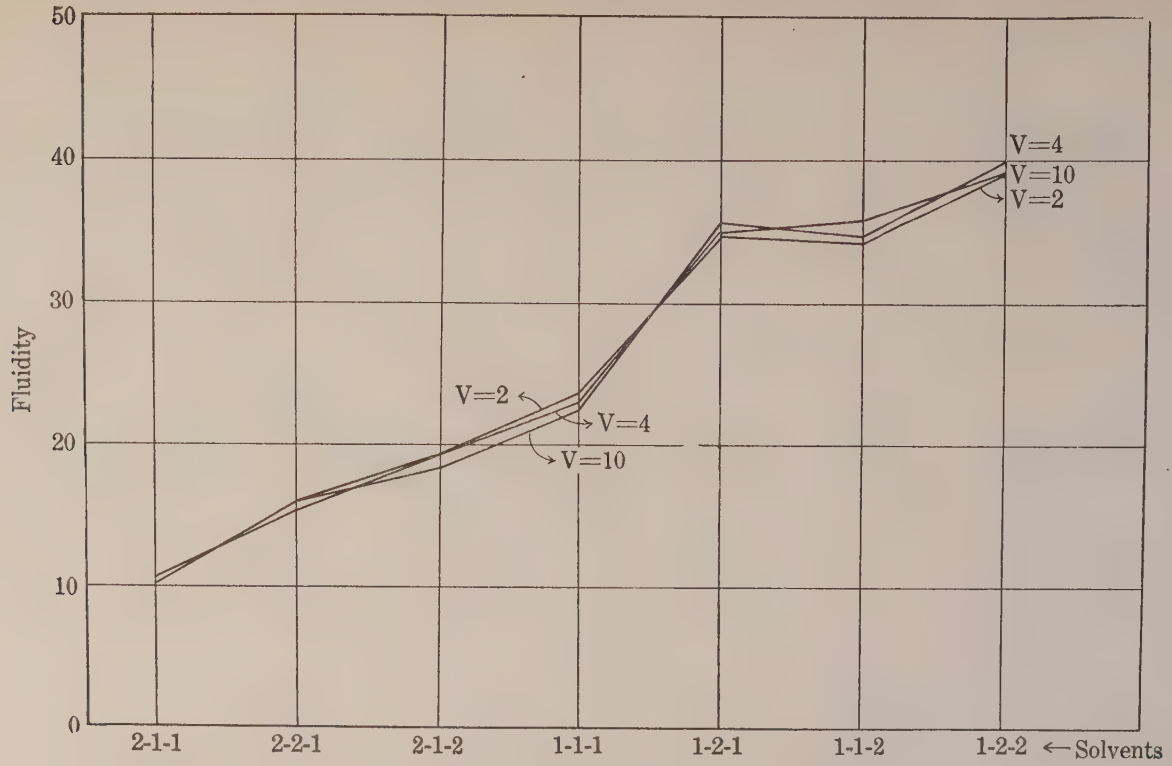


Figure 2.—Fluidity of ammonium iodide in glycerol, acetone, and water at 25°.

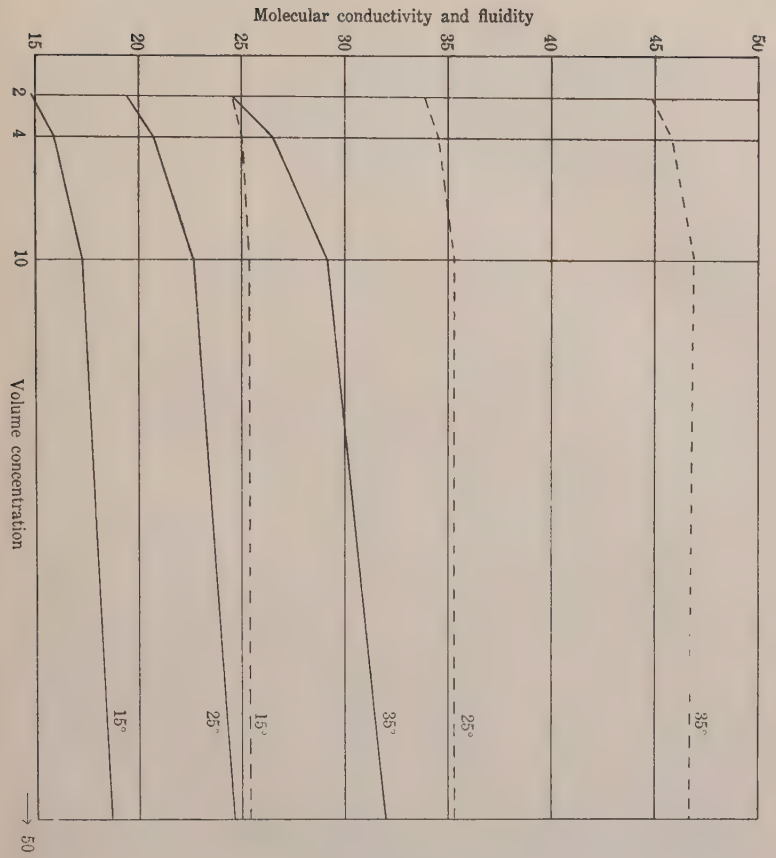


Figure 3.—Conductivity and fluidity of rubidium bromide in the 1-2-1 solvent at 15°, 25°, and 35°.
—— = Conductivity curves.
- - - - = Fluidity curves.

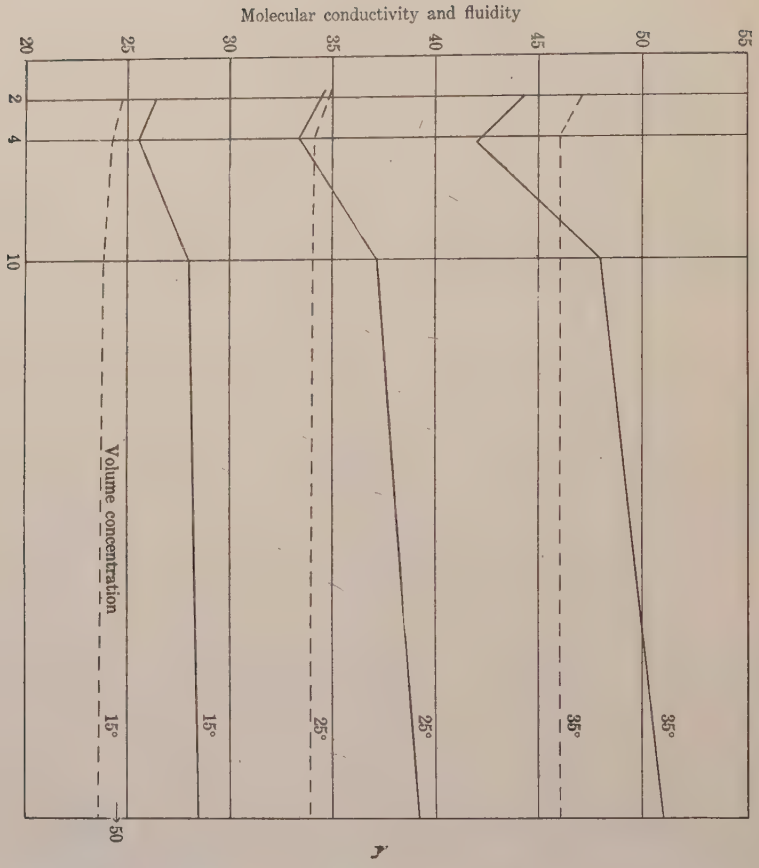


Figure 4.—Conductivity and fluidity of rubidium bromide in the 1-1-2 solvent at 15°, 25°, and 35°.
—— = Conductivity curves.
- - - - = Fluidity curves.

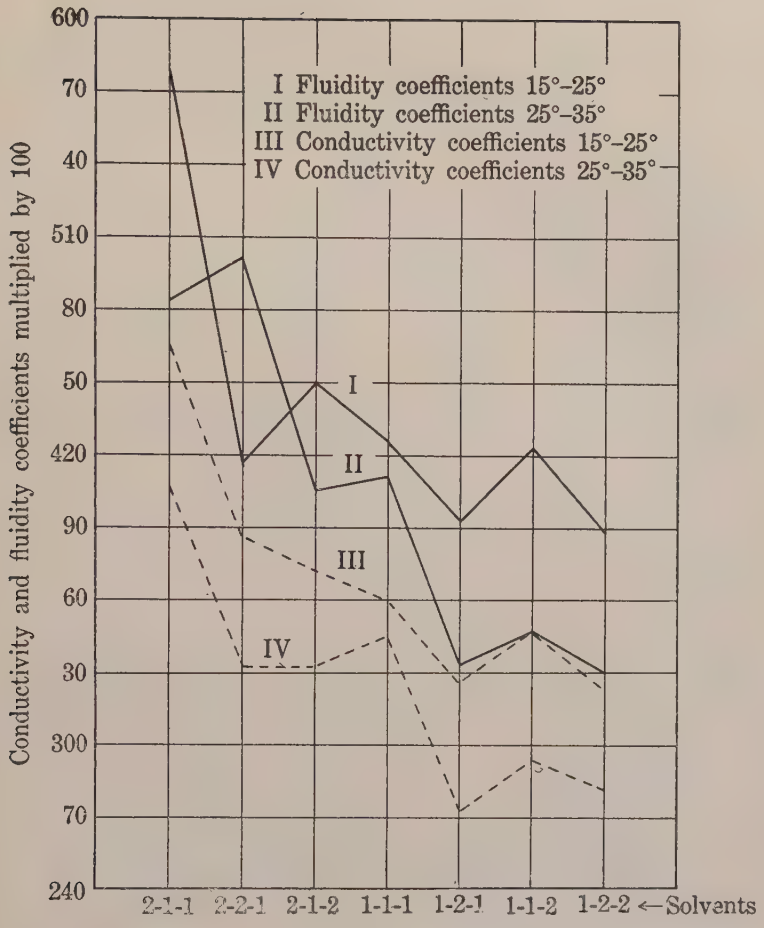


Figure 5.—Conductivity and fluidity temperature coefficients for N/10 solution of ammonium iodide in glycerol, acetone, and water.

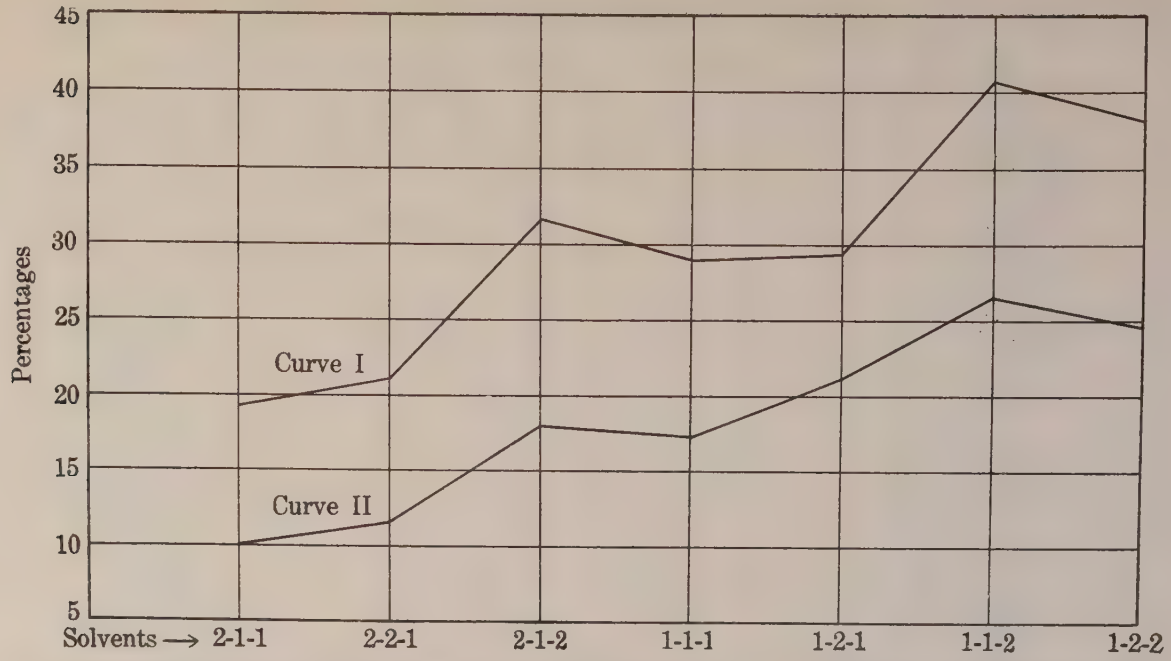


Figure 6.—Ordinates are Percentages by Which Measured Conductivity and Fluidity Differ from the Values Calculated from Averages.
Curve I. Calculated from conductivity of Rb I at 25°.
Curve II. Calculated from fluidity of solvents at 25°.

# DISCUSSION OF RESULTS

Dr. Paul B. Davis made viscosity measurements of all the solvents and solutions that have been used in this investigation. As viscosity and conductivity are so intimately related, reference is made to his work throughout this discussion and curves plotted from his data are published for comparison, in addition to the conductivity curves.

Table I gives the specific conductivity of the seven solvents used, and Tables II to LIII give the molecular conductivity, temperature coefficients in conductivity units and percentages, of ammonium iodide, ammonium bromide, rubidium iodide and rubidium bromide in each of the solvents.

The specific conductivity of the 1-1-1 solvent is about 3000 times that calculated by averaging the specific conductivities of each of the constituents. Jones and Davis[1] have noted that in mixtures of glycerol and water containing 50 per cent. and 25 per cent. glycerol, the specific conductivity was higher than for pure water. Their explanation is that the OH ion is split off; i. e., the glycerol is dissociated by the action of the water. Jones and Bingham[2] show that the molecular conductivity of a N/200 solution of potassium iodide is about the same as in pure water. Since the fluidity of acetone is about two and a half times that of water, the dissociating action of acetone would be of the order of 40 per cent. that of water.

The relative association factors of water and acetone would lead to the same conclusion. While this conclusion may not be quantitatively accurate it is safe to say that acetone is a strong dissociating agent. It is therefore probable that the OH ions are split off from the glycerol by the combined action of the water and acetone. This dissociation would explain the very high specific conductivities of the solvents used in this investigation, compared with those calculated by averaging the specific conductivities of the constituents.

The fluidity of the 1-1-1 solvent is about one-sixth that calculated by averages, while the specific conductivity is, as noted above, about 3000 times that calculated by the same method;

1, Carnegie Institute of Washington, Publication No. 210
2, Carnegie Institute of Washington, Publication No. 180

hence the specific conductivity of the solvent is roughly 18000 times that which would be expected. While these figures can be considered only as a very rough approximation, they indicate a very large dissociation of the glycerol in these ternary mixtures.

Further evidence for this view is obtained from the 1-2-2 solvent, whose specific conductivity exceeds by a much larger amount that calculated by the method indicated above. The relative amounts of acetone and water are much larger in the 1-2-2 solvent than in the 1-1-1, hence a larger dissociation of the glycerol should be expected from the law of mass action.

Jones and Lindsay,[3] continuing the investigation of the phenomenon of minima in conductivity curves observed by Zelinsky and Krapiwin and by Cohen, advanced the theory, based on the hypothesis of Dutoit and Aston, that the decrease in conductivity and fluidity in solvents consisting of mixtures of associated liquids, was due to the fact that each liquid decreased the association of the other, thus decreasing the size of the ultimate unit particles composing the solvent, and increasing the amount of frictional surface between them.

The negative viscosity caused by some salts of rubidium, caesium, and ammonium is also satisfactorily explained by this theory of frictional surface in the solution. A large amount of experimental evidence has been published by Jones and his collaborators.[4] With these two conceptions in mind; i. e., the effect of the size of the particles and the decrease in association of one associated liquid by another, it seems clear that by the addition of a third associated liquid to such a binary mixture, the decrease in association would be carried farther, resulting in an increased amount of frictional surface and decreased fluidity. If the unit particles in the acetone were much larger than those already in the binary mixture, the fluidity of the resulting ternary mixture would be increased. This is not probable as acetone is an associated liquid, and the presence of three such liquids, each decreasing the association of the others would, it is reasonable to conclude, result in a large increase in the number of smaller particles. All conductivity and fluidity measurements made during this investigation support this view. The comparisons named below furnish some of the evidence for these conclusions.

To compare the results obtained with those calculated by averages, consider the data obtained by Jones and Davis[5] with glycerol-water mixtures, and by Jones, Davis and Hughes[6] with ace-

3, Carnegie Institute of Washington, Publication No. 80
4, Carnegie Institute of Washington, Publication Nos. 80 and 180
5, Carnegie Institute of Washington, Publication No. 180
6, Carnegie Institute of Washington, Publication No. 210

tone-water mixtures. They used rubidium bromide in the following solvents:

75 per cent. Glycerol and 25 per cent. Water.....A
75 per cent. Acetone and 25 per cent. Water.....B
50 per cent. Glycerol and 50 per cent. Water.....C
50 per cent. Acetone and 50 per cent. Water.....D

It should be noted that the action of all four salts used in this investigation do not differ widely in the same solvents. The average obtained with the 2-1-1 and 1-2-1 solvents can be compared with the A and B solvents, since all contain 25 per cent. water. The 75 per cent. of the ternary mixture is, by averaging the 1-2-1 and 2-1-1 solvents, equally divided between glycerol and acetone. Solvents C and D can be compared with the 1-1-2 solvent since all contain 50 per cent. water. The following data for an N/4 solution of rubidium bromide illustrate the comparison:

Conductivity in 75 per cent. glycerol, 25 per cent. water..... 5.43
Conductivity in 75 per cent. acetone, 25 per cent. water.....39.10

Average .....22.27

Conductivity in 2-1-1 solvent .....11.16
Conductivity in 1-2-1 solvent .....20.74

Average .....15.95

15.95 is only 72 per cent. of 22.27.

Conductivity in 50 per cent. glycerol, 50 per cent. water.....23.33
Conductivity in 50 per cent. acetone, 50 per cent. water.....57.90

Average .....40.62

Conductivity in 1-1-2 solvent .....33.45

33.45 is only 82 per cent. of 40.62.

Fig. 1 shows the conductivity curves of ammonium iodide in the ternary solvents at 25°; and Fig. 2 shows the corresponding fluidity curves. While these curves have the same general character, some marked differences are noticeable. The fluidities of glycerol, water and acetone at 25° are respectively 0.17 112.30 and 288.95. The figures for glycerol and water are taken from the data of Jones and Davis, and acetone from the data of Jones and Bingham.[7]

See page 7 for association factors and dielectric constants of these liquids. Dissociation is either roughly proportional to the dielectric constants as stated by the Thompson[8]-Nernst[9] theory,

7. Carnegie Institute of Washington, Publication No. 80
8 Phil, Mag, 36, 320 [1893]
9. Zeit Phys. Chem. 13 531 (1894)

or to the association factors as stated by the Dutoit and Aston.[10] theory. A consideration of these theories with the fluidities will explain all cases of non-parallelism in these two sets of curves. These explanations cannot approach a quantitative basis because reducing the association affects both the fluidity and dissociation, and the relative effect on each is not known.

As an illustration, consider the change from the 1-1-1 solvent to the 1-2-1. The fluidity increases five times as much as the conductivity. The changes affecting fluidity are as follows: the water changes from 33 per cent. to 25 per cent. causing a small reduction; glycerol changes from 33 per cent. to 25 per cent. causing a rather large increase, while acetone changes from 33 per cent. to 50 per cent. causing a very large increase. The change in water would reduce the conductivity, while the changes in acetone and glycerol would increase the conductivity much less than the fluidity. A consideration of the above details makes it clear that a much larger increase in fluidity than conductivity would be expected.

Other changes from one solvent to another can be explained by similar considerations.

Figs. 3 and 4 show fluidity and molecular conductivity curves for rubidium bromide in the 1-2-1 and the 1-1-2 solvents at 15°, 25°, and 35°. Jones, Davis and Hughes have shown that for glycerol-water mixtures and acetone-water mixtures, temperature coefficients of fluidity are larger than for conductivity, because increasing temperature decreases the dissociation. These curves show that the same relation is true of the ternary solvents. Sufficiently dilute solutions have not been used in this work to determine accurately the dissociation. The data obtained by Jones and Bingham, and the work on glycerol-water and acetone-water mixtures indicate that solutions more dilute than N/1600 must be used. Decrease in dissociation from 15° to 35° is slight, and is not enough to explain the difference between the fluidity and conductivity coefficients. Rubidium and ammonium salts are not in the class that form complex solvates, yet of the known factors which affect conductivity the formation of solvates is the only one which can explain the point here raised. If a solvate is formed and the rise in temperature reduces its complexity less than it increases the fluidity, it is a satisfactory explanation. In this connection it should be noted that Jones and Guy[11] have found some evidence for the formation of glycerolates by sodium and potassum salts. The acetone-water investigation shows some

10, Compt, Rend, 240 [1897]

11, Carnegie Institute of Washington Publication No. 180

evidence for the formation of solvates by rubidium salts in a mixed solvent. Another factor which should be investigated is the polymerizing action of acetone, and the effect of temperature on the complexity of the polymers.

It should be noted that Figs. 3 and 4 show two distinct types of curves. In Fig. 3 both conductivity and fluidity curves are regular, while in Fig. 4 both curves show a minimum. The minimum occurs at the N/4 point. The effect in conductivity of the usual increase in dissociation from N/2 to N/4 is overcome by the decrease in fluidity, thus producing the minimum point. From N/4 to N/10 there is little change in fluidity, hence the increase in dissociation gives the curves a sharp upward turn. In Fig. 3 the influence of increasing fluidity and dissociation work together producing a convex curve.

Going back to the fundamental cause; why do these rubidium and ammonium salts cause conductivity minima and also fluidity minima in some of these ternary solvents and not in others? In some cases, a flat curve or a straight line is produced. In all such cases the fluidity coefficients are negative. These negative coefficients occur only with the solvents containing 40 per cent. and 50 per cent. acetone. The first suggestion would be that it was due to some specific effect of acetone on the fluidities of these solvents, but a study of them and also of Fig. 6 makes this view untenable. The explanation suggested is the polymerizing action of acetone. The normal action of these salts is to produce positive fluidity coefficients on account of large molecular volumes. The formation of a polymer would reduce the number of molecules and hence weaken or overcome the action that results in these positive coefficients. Jones and Mahin have shown that cadmium iodide, lithium acetate and lithium nitrate polymerize in acetone. More data on the polymerization of inorganic salts is desirable.

Fig. 5 shows for comparison, the temperature coefficients for conductivity and fluidity for an N/10 solution of ammonium iodide in the ternary solvents for 15° to 25° and 25° to 35°. There is a striking similarity between the curves for the conductivity and fluidity coefficients. They are lower for the higher range in temperature as would be expected from the work in other solvents. The conductivity temperature coefficients are very close to those calculated from averages from the data of the glycerol-water and acetone-water investigations. As glycerol has a much higher conductivity temperature coefficient than either acetone or water, the solvents containing the largest percentage of glycerol should

have the highest coefficients. The curves harmonize with this fact.

N/800 solutions were the most dilute used in this work. The data show that the amount of dissociation cannot be calculated with certainty, but it indicates higher dissociation values than those calculated by averages from glycerol-water and acetone-water data.

Conductivity and fluidity in these ternary solvents is much below the average. These considerations emphasize the fact that fluidity outweighs all the other factors that affect conductivity.

As already noted, the fluidity data indicate that association is more reduced in the ternary than in the binary solvents, but a decreased dissociation is not indicated as might be expected from the deduction of Jones and Lindsay.

It is important to determine what effect glycerol, acetone and water have on each other when constituting a ternary mixture. This investigation has shown that the properties of these ternary solvents are widely different from those which can be calculated from averages. The curves of Fig. 6 are made to show the differences between the measured and calculated conductivities and fluidities. To illustrate: the fluidity of the 2-1-1 solvent is 10.31 at 25°. Calculated by averages it is 100.4. The measured is thus 10 per cent. of the calculated, hence 10 is the ordinate for the 2-1-1 point. The data for making the conductivity curves is not as full as could be desired. For acetone the value is taken from the data of Jones and Bingham[12] on potassium iodide for an N/200 solution at 25°. The rubidium bromide in glycerol and in water are taken from the data of Jones and Davis.[13] The action of potassium and rubidium salts in relation to conductivity are nearly enough alike for the purpose of this comparison. The 2-1-1 ordinate shows that the measured conductivity is 19.2 per cent. of the calculated. That the curves have the same character is another evidence of the close relation existing between conductivity and fluidity.

In Fig. 6 the solvents are arranged from left to right in the order of the percentage of glycerol they contain. Hence the curves show that the more glycerol the solvents contain, the more the conductivity and fluidity values depart from the calculated average. The theory first announced by Jones and Veazey state that viscosity is due to the friction between the particles of the liquid. It is clear that the smaller the particles, the greater will be the amount of frictional surface between them, hence the

12. Carnegie Institute of Washington Publication No. 80.
13. Carnegie Institute of Washington Publication No. 180.

greater the viscosity of any homogeneous liquid, the smaller must be the particles composing it. The density of the liquid should also affect the viscosity. The densities of glycerol, water and acetone are 1.26, 1.00 and 0.79 respectively, while the fluidities are in the ratio 1:702:1741; hence the variation in density is so small in comparison with the variation in fluidity that the former can be neglected. It seems probable that there is one other important factor that governs fluidity, which must be considered in addition to the size of the particle. The particle in a pure homogeneous liquid would be either one molecule or an association of molecules.

The conception of molecular volume is opposed to the view that the glycerol particle is smaller than that of acetone or water. Acetone and glycerol have the same molecular volume, i. e., 73 and water has 18, calculated for the simple molecule. Considering the association factors, the molecular volumes are as follows: glycerol 150, acetone 92 and water 72. From the latter consideration glycerol has the larger molecular volume hence, should have the highest fluidity, which is contrary to the facts. The error probably arises from the use of the density factor in calculating molecular volume. The density of the liquid is affected by both the density of the molecules and the spaces between them. The kinetic molecular hypothesis states that for a gas the space betwen the molecules is much greater than that occupied by the molecules. For a liquid the intermolecular space is less than for a gas, and for a solid less than for a liquid. For liquids it seems reasonable to believe that the density of the liquid gives no idea of the density of the molecule or the space betwen them; and it is the latter factor of intermolecular space as well as the size of the particle that must be considered as the chief factor governing fluidity Hence the conception of molecular volume as applied to liquids is not opposed to the theory that fluidity depends on the frictional surface between the particles or molecular associations, and the necessary corellary that the amount of frictional surface depends on the size of the particles. It should be noted in this connection that as it is clear that the intermolecular space of a gas is the most important factor affecting its viscosity, it is reasonable to believe that the same factor must be considered in studying the viscosity or fluidity of liquids, although it is relatively less important than for gasses. It is probable that the present conception of molecular volume as applied to solids is approximately correct since the intermolecular space may be so small that it can be neglected.

## Summary.

1. The conductivities of the ternary solvents make it probable that water and acetone act as dissociating agents on glycerol.

2. The decrease in the association of one associated liquid by another associated liquid is much larger in a ternary than in a binary mixture, thus producing decreased values in conductivity and fluidity.

3. A consideration of the hypotheses of Dutoit and Aston and of Thompson-Nernst, together with the fluidities of glycerol, acetone and water, explain the differences between the conductivity and fluidity curves in these ternary solvents.

4. Temperature coefficients for fluidity are larger than for conductivity as in binary solvents. The formation of solvates is a possible explanation of the difference between these coefficients.

5. The minimum point which occurs in some of the conductivity curves is explained by considering the fluidity of the solution.

6. A possible explanation of the fluidity changes which produce minima in the conductivity and fluidity curves is the polymerization of the salts by the acetone.

7. The conductivity and fluidity values of the solvents containing the largest percentage of glycerol are farthest below these values calculated by averages.

8. The conductivity temperature coefficients are about the same as those calculated by averages.

9. This investigation emphasizes the fact, already known, that fluidity outweighs all the other factors affecting conductivity.

10. The conditions governing viscosity in a pure homogeneous liquid are discussed from a physical point of view.

# PART II

## THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN BINARY AND TERNARY SALTS IN FORMAMID

## INTRODUCTION

The only investigation, previous to this one, which attempted to determine the properties of formamid as a solvent was carried out by Walden.[1] He measured the conductivity of a few solutions in this solvent, but relied chiefly on the freezing point method to determine dissociation. The average specific conductivity of the formamid he used was $7.5 \times 10^{-4}$. He considered the correction for the solvent so large that the results of the conductivity method did not have satisfactory accuracy. He determined the dissociation of several inorganic salts and potassium iodide, boric acid, hydrobromic acid, cacodylic acid, trichlor—and tribromacetic acid. He found that formamid was a stronger dissociating solvent than water in all cases in which the electrolyte did not combine with, or react with the solvent.

1, Bulletin of the Imperial Academy of Sciences of Petrograd, Nov, 1911--Reprint in German,

# FORMAMID AS A SOLVENT

In some respects water and formamid are similar solvents. As Walden points out, both are miscible with methyl and ethyl alcohols, and are very nearly non-miscible with benzol, hexane, chloroform, chlorbenzol and nitrobenzol. Such salts as antimony trichloride are hydrolysed. Bruni and Manuelli[2] show that these salts undergo in formamid an analogous decomposition. The following compounds or mixtures of them are formed:

$SbCl_2(HCONH)$, $SbCl(HCONH)_2$ and $Sb(HCONH)_3$.

Salts of some of the heavy metals react with formamid forming *amidates*, analogous to hydroxides. In some cases, the *amidate* unites with the excess of the solvent, holding one or more molecules of formamid, as water of crystallization is held in combination. The following have been isolated by Röhler[3]:

$(HCONH)_2$ Cu-$2HCONH_2$, $(HCONH)_2$ Ni-$2HCONH_2$ $(HCONH)_2$ Co-$2HCONH_2$, $(HCONH)_2$ Zn-$2HCONH_2$ Pb$(HCONH)_2$ and Pb $Cl_2$ $HCONH_2$.

Formamid also acts like water in uniting with the halogen acids at low temperatures, forming crystalline compounds. $HCONH_2$-3HCl and $2HCONH_2$-HBr have been isolated by Röhler. B. Menschatkin[4] states that acetamid forms compounds analogous to those of formamid which have been mentioned.

In table I are given the association factors of formamid found by Turner and Merry.[5] In table II are given the association factors, dielectric constants and viscosity of formamid and several other solvents, all of which, except hydrocyanic acid have been investigated in this laboratory. The dielectric constant and association factor of formamid were determined by Walden. The figures for the other solvents are from the work of Drude at 18°. The association factors, except for formamid, were obtained by Ramsey and Shields. The viscosity values were obtained by Jones and his co-workers.

2, Zeit, Elck, Chem, 11-554 (1905)
3, Zeit, Elek, Chem, 16--428 (1910)
4, Jour, Russ, Chem. Ges, 40--1415 (1908,) 39--102 (1907)
5, Jour, Chem, Soc, 97--2076 (1910)

**TABLE I.**

| Temperature. | Association Factor. |
|---|---|
| 30° | 6.18 |
| 45° | 5.76 |
| 60° | 4.85 |
| 75° | 3.34 |

**TABLE II.**

| Solvent | Dielectric Constant | Association Factor | Viscosity at 25° |
|---|---|---|---|
| HCN | 95 | .... | ..... |
| $HCONH_2$ | 84 | 6.18 | 0.0326 |
| $H_2O$ | 81.7 | 3.81 | 0.0089 |
| $CH_3OH$ | 32.5 | 3.43 | 0.0056 |
| $C_2H_5OH$ | 21.7 | 2.74 | 0.0111 |
| $C_3H_5(OH)_3$ | 16.5 | 1.80 | 5.854 |
| $CH_3$-CO-$CH_3$ | 20.7 | 1.26 | 0.0035 |

Walden has determined the Freezing Point Constant of formamid to be 35.0.

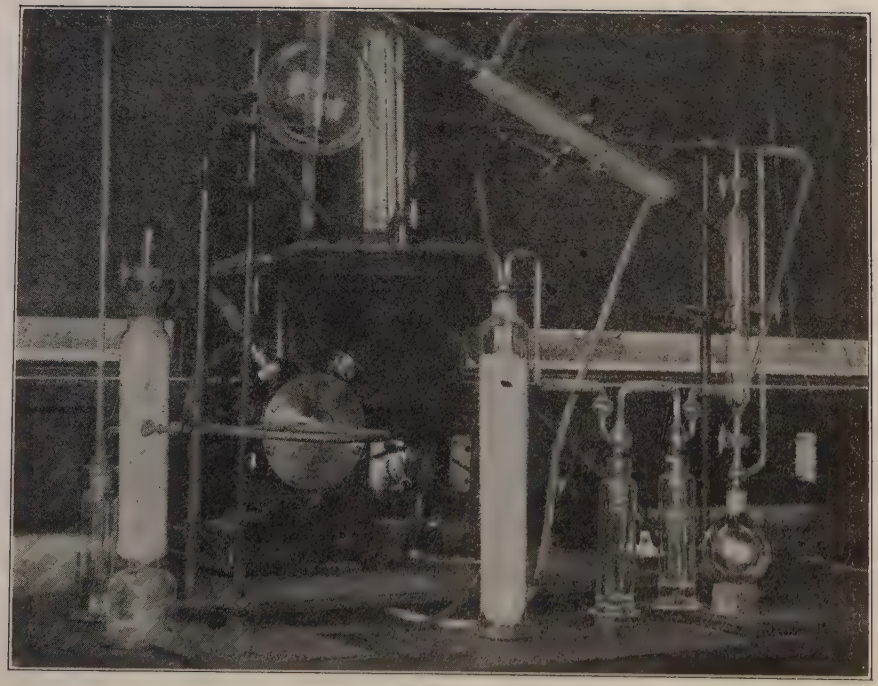

Plate I.

# EXPERIMENTAL

### Apparatus and Methods.

Viscosity measurements of all solvents and solutions used in this investigation were made by Davis.

The apparatus and methods employed for viscosity and conductivity measurements were the same as described in the first part of this dissertation for the solutions in mixed solvents.[1] Plate I shows the arrangement of the vacuum distillation apparatus. The Gaede Vacuum Pump was made by E. Seybold of Cologne and will reduce pressure to 0.006 millimeters of mercury. It was driven by a 1/12 horse power direct current motor designed to run 1725 revolutions per minute. The speed was regulated by a small rheosat. Between the receiver and the pump were two bottles and a soda lime tower. One of the bottles contained sulphuric acid. The other was empty and served as a trap in case of back pressure. The acid and soda lime protect the pump from alkaline and acid vapors. Additions can be made to the distilling flask, and the distillate withdrawn from the receiver without interfering with the vacuum.

The viscosity of formamid is about 3.6 times that of water. The bumping which accompanies the vacuum distillation of such a viscous liquid as formamid was prevented by passing through a current of dry air. Great care was necessary in drying the air, since slight traces of moisture cause the hydrolytic decomposition of formamid. The air was dried in a tower filled with calcium chloride and soda lime, two bottles containing sulphuric acid and a phosphorus pentaoxide tube. This drying train is partly shown on the left of Plate I. In the evacuated system are four stop-cocks, and five ground-glass stoppers, two rubber stoppers and seven rubber tube connections. Under these unfavorable conditions and with a current of dry air running through, the Gaede pump maintained a pressure of two to three millimeters during distillattion.

1, For a more complete description and illustration of details of constant temperature baths, gas regulators and thermostats, see Publication No, 210 of the Carnegie Institute of Washington

### The Solvent.

Kalbaum's formamid, having an average specific conductivity of $6.7 \times 10^{-3}$ was the material which we purified. The hydrolysis of formamid causes the formation of formic acid, ammonium formate and ammonia. It is probable that the high specific conductivity noted above was due to the presence of small amounts of these decomposition products. After four or five distillations, the formamid was sufficiently pure to use for preparing solutions. From the original amount of formamid, about 35 per cent. was obtained, having sufficiently low conductivity for use. After measurements of conductivity and viscosity were completed, the solutions were distilled. A solvent suitable for use was obtained usually after three distillations. The specific conductivity of the solvent varied from $4.71 \times 10^{-5}$ to $1.37 \times 10^{-5}$ at 25°. We do not know at present what minimum limit can be reached for the specific conductivity of formamid at 25°. Small lots were obtained having the value $0.48 \times 10^{-5}$ which is equal to about three times the value of the ordinary conductivity water used in this laboratory.

## TABLE III.

### Molecular Conductivity and Dissociation of Potassium Iodide at 15°-25°-35°.

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 2 | 14.42 | 18.67 | 23.29 | 70.7 | 71.0 | 71.0 |
| 4 | 16.32 | 21.05 | 26.34 | 80.0 | 80.1 | 80.3 |
| 10 | 18.23 | 23.45 | 29.21 | 89.4 | 89.2 | 89.0 |
| 50 | 19.25 | 24.87 | 31.03 | 94.4 | 94.6 | 94.5 |
| 200 | 20.39 | 26.28 | 32.81 | 100.0 | 100.0 | 100.0 |
| 400 | 20.26 | 26.29 | 32.82 | | | |
| | K 2.23 x $10^{-5}$ | 2.83 x $10^{-5}$ | 3.48 x $10^{-5}$. | | | |

## TABLE IV.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0295 | 0.0247 | 0.425 | 0.462 |
| 4 | 0.0290 | 0.0251 | 0.473 | 0.529 |
| 10 | 0.0286 | 0.0246 | 0.522 | 0.576 |
| 50 | 0.0292 | 0.0248 | 0.562 | 0.616 |
| 200 | 0.0289 | 0.0248 | 0.589 | 0.653 |

## TABLE V.

### Molecular Conductivity and Dissociation of Sodium Iodide at 15°-25°-35°.

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 2 | 11.92 | 15.71 | 20.01 | 64.7 | 65.6 | 66.1 |
| 4 | 14.17 | 18.57 | 23.59 | 76.9 | 77.5 | 78.0 |
| 10 | 15.91 | 20.67 | 26.05 | 86.3 | 86.3 | 86.1 |
| 50 | 17.17 | 22.33 | 28.17 | 93.2 | 93.2 | 93.1 |
| 200 | 18.27 | 23.80 | 29.98 | 99.1 | 99.3 | 99.1 |
| 400 | 18.43 | 23.96 | 30.25 | 100.0 | 100.0 | 100.0 |
| | K 2.23 x $10^{-5}$ | 2.83 x $10^{-5}$ | 3.48 x $10^{-5}$. | | | |

K in table III and following tables is the specific conductivities of the solvent at 15°--25°--35°

## TABLE VI.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0318 | 0.0274 | 0.379 | 0.430 |
| 4 | 0.0311 | 0.0270 | 0.440 | 0.502 |
| 10 | 0.0299 | 0.0260 | 0.476 | 0.538 |
| 50 | 0.0301 | 0.0262 | 0.516 | 0.584 |
| 200 | 0.0303 | 0.0260 | 0.553 | 0.618 |
| 400 | 0.0300 | 0.0263 | 0.553 | 0.629 |

## TABLE VII.

### Molecular Conductivity and Dissociation of Lithium Nitrate at 15°-25°-35°.

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 2 | 12.16 | 15.57 | .... | 66.0 | 65.8 | .... |
| 4 | 14.10 | 18.07 | ... | 76.5 | 76.4 | ... |
| 10 | 16.11 | 20.58 | 25.54 | 87.5 | 87.0 | 86.9 |
| 50 | 17.38 | 22.29 | 27.68 | 94.4 | 94.2 | 94.1 |
| 200 | 18.42 | 23.66 | 29.34 | 100.0 | 100.0 | 99.8 |
| 400 | 18.23 | 23.63 | 29.40 | | | 100.0 |
| | K 2.19 x $10^{-5}$ | | 2.78 x $10^{-5}$ | | 3.38 x $10^{-5}$. | |

## TABLE VIII.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0280 | ..... | 0.341 | ..... |
| 4 | 0.0281 | ..... | 0.397 | ..... |
| 10 | 0.0277 | 0.0241 | 0.447 | 0.496 |
| 50 | 0.0283 | 0.0242 | 0.491 | 0.539 |
| 200 | 0.0284 | 0.0240 | 0.524 | 0.568 |
| 400 | 0.0296 | 0.0244 | 0.540 | 0.577 |

## TABLE IX.

**Molecular Conductivity and Dissociation of Rubidium Nitrate at 15°-25°-35°.**

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 4 | 16.20 | 20.79 | 25.85 | 77.7 | 77.6 | 77.6 |
| 10 | 18.85 | 24.07 | 30.00 | 90.4 | 89.8 | 90.1 |
| 50 | 20.22 | 25.97 | 32.23 | 97.0 | 96.9 | 96.8 |
| 100 | 20.85 | 26.80 | 33.31 | 100.0 | 100.0 | 100.0 |
| 200 | 20.76 | 26.68 | 33.02 | | | |
| | K 2.47 x $10^{-5}$ | | 3.17 x $10^{-5}$ | | 3.94 x $10^{-5}$. | |

## TABLE X.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 4 | 0.0283 | 0.0243 | 0.459 | 0.506 |
| 10 | 0.0277 | 0.0246 | 0.522 | 0.593 |
| 50 | 0.0284 | 0.0241 | 0.575 | 0.626 |
| 100 | 0.0285 | 0.0243 | 0.595 | 0.651 |

## TABLE XI.

**Molecular Conductivity and Dissociation of Rubidium Iodide at 15°-25°-35°.**

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 2 | 14.73 | 19.01 | 23.78 | 72.4 | 72.0 | 72.2 |
| 4 | 16.87 | 21.71 | 27.21 | 82.9 | 82.2 | 82.6 |
| 10 | 18.60 | 24.00 | 29.83 | 91.4 | 90.9 | 90.5 |
| 50 | 19.59 | 25.27 | 31.49 | 96.3 | 95.7 | 95.6 |
| 100 | 20.23 | 26.06 | 32.52 | 99.5 | 98.7 | 98.7 |
| 200 | 20.34 | 26.41 | 32.95 | 100.0 | 100.0 | 100.0 |
| | K 3.68 x $10^{-5}$ | | 4.71 x $10^{-5}$ | | 5.87 x $10^{-5}$. | |

## TABLE XII.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0290 | 0.0251 | 0.428 | 0.477 |
| 4 | 0.0287 | 0.0253 | 0.484 | 0.550 |
| 10 | 0.0290 | 0.0243 | 0.540 | 0.583 |
| 50 | 0.0290 | 0.0246 | 0.568 | 0.622 |
| 100 | 0.0288 | 0.0248 | 0.568 | 0.646 |
| 200 | 0.0298 | 0.0248 | 0.607 | 0.654 |

## TABLE XIII.

### Molecular Conductivity and Dissociation of Caesium Chloride at 15°-25°-35°.

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 4 | 16.83 | 21.69 | 27.15 | 78.6 | 78.8 | 78.7 |
| 10 | 18.75 | 24.09 | 30.03 | 87.6 | 87.5 | 87.1 |
| 200 | 21.40 | 27.54 | 34.49 | 100.0 | 100.0 | 100.0 |
| 400 | 21.06 | 27.15 | 34.11 | | | |
| | K 1.34 x $10^{-5}$ | | 1.72 x $10^{-5}$ | 2.10 x $10^{-5}$. | | |

## TABLE XIV.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 4 | 0.0289 | 0.0252 | 0.486 | 0.546 |
| 10 | 0.0285 | 0.0247 | 0.534 | 0.594 |
| 200 | 0.0287 | 0.0252 | 0.614 | 0.695 |
| 400 | 0.0289 | 0.0256 | 0.609 | 0.696 |

## TABLE XV.

**Molecular Conductivity and Dissociation of Caesium Nitrate at 15°-25°-35°.**

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 4 | 17.00 | 21.79 | 27.10 | 78.2 | 78.1 | 78.3 |
| 10 | 18.90 | 24.23 | 29.92 | 86.9 | 86.8 | 86.4 |
| 100 | 21.36 | 27.42 | 33.99 | 98.2 | 98.3 | 98.2 |
| 200 | 21.75 | 27.90 | 34.61 | 100.0 | 100.0 | 100.0 |
| 400 | 21.59 | 27.64 | 34.43 | .... | ..... | ..... |
| | K 1.34 x $10^{-5}$ | | 1.72 x $10^{-5}$ | | 2.10 x $10^{-5}$. | |

## TABLE XVI.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 4 | 0.0282 | 0.0244 | 0.479 | 0.531 |
| 10 | 0.0282 | 0.0235 | 0.533 | 0.569 |
| 100 | 0.0284 | 0.0240 | 0.606 | 0.657 |
| 200 | 0.0283 | 0.0241 | 0.615 | 0.671 |
| 400 | 0.0280 | 0.0246 | 0.605 | 0.679 |

## TABLE XVII.

**Molecular Conductivity and Dissociation of Potassium Sulphocyanate at 15°-25°.35°.**

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 2 | 15.15 | 19.10 | 24.28 | 70.0 | 69.2 | 70.4 |
| 4 | 17.42 | 22.31 | 27.87 | 80.6 | 80.8 | 80.8 |
| 10 | 19.04 | 24.38 | 30.35 | 88.0 | 88.3 | 88.0 |
| 50 | 20.03 | 25.61 | 32.16 | 92.6 | 92.8 | 93.3 |
| 200 | 21.21 | 27.19 | 33.89 | 98.1 | 98.5 | 98.3 |
| 400 | 21.62 | 27.60 | 34.47 | 100.0 | 100.0 | 100.0 |
| | K 1.01 x $10^{-5}$ | | 1.37 x $10^{-5}$ | | 1.69 x $10^{-5}$. | |

## TABLE XVIII.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 2 | 0.0261 | 0.0271 | 0.395 | 0.518 |
| 4 | 0.0281 | 0.0249 | 0.489 | 0.556 |
| 10 | 0.0280 | 0.0245 | 0.534 | 0.597 |
| 50 | 0.0279 | 0.0256 | 0.558 | 0.655 |
| 200 | 0.0282 | 0.0246 | 0.598 | 0.670 |
| 400 | 0.0277 | 0.0249 | 0.598 | 0.687 |

## TABLE XIX.

### Molecular Conductivity of Sodium Chromate at 15°-25°-35°.

| | Molecular Conductivity. | | |
|---|---|---|---|
| V. | 15° | 25° | 35° |
| 10 | 25.57 | 33.66 | 42.66 |
| 50 | 31.46 | 41.48 | 52.18 |
| 200 | 34.34 | 44.82 | 56.38 |
| 400 | 39.00 | 50.79 | ..... |
| 800 | 42.64 | 55.07 | 69.16 |
| 1600 | 72.06 | 93.51 | 116.44 |
| K | $1.30 \times 10^{-5}$ | $1.65 \times 10^{-5}$ | $2.03 \times 10^{-5}$. |

## TABLE XX.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 10 | 0.0316 | 0.0267 | 0.809 | 0.900 |
| 50 | 0.0319 | 0.0258 | 1.002 | 1.070 |
| 200 | 0.0305 | 0.0258 | 1.048 | 1.156 |
| 400 | 0.0302 | ..... | 1.179 | ..... |
| 800 | 0.0292 | 0.0256 | 1.243 | 1.409 |
| 1600 | 0.0298 | 0.0245 | 2.145 | 2.293 |

## TABLE XXI.

**Molecular Conductivity of Mercuric Chloride at 15°-25°-35°.**

| | Molecular Conductivity. | | |
|---|---|---|---|
| V. | 15° | 25° | 35° |
| 4 | 0.43 | 0.59 | 0.83 |
| 10 | 0.63 | 0.87 | 1.27 |
| 50 | 1.09 | 1.56 | 2.22 |
| 200 | 1.74 | 2.53 | 3.68 |
| 400 | 2.73 | 4.15 | 5.82 |
| 1000 | .... | 134.49 | .... |
| 1600 | .... | 101.13 | .... |
| 3200 | .... | 75.35 | .... |

K 1.30 x $10^{-5}$ 1.65 x $10^{-5}$ 2.03 x $10^{-5}$.

## TABLE XXII.

**Temperature Coefficients.**

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 4 | 0.0372 | 0.0407 | 0.016 | 0.024 |
| 10 | 0.0381 | 0.0460 | 0.024 | 0.040 |
| 50 | 0.0431 | 0.0423 | 0.047 | 0.066 |
| 200 | 0.0437 | 0.0455 | 0.076 | 0.115 |
| 400 | 0.0520 | 0.0402 | 0.142 | 0.167 |

## TABLE XXIII.

**Molecular Conductivity and Dissociation of Cobalt Bromide at 15°-25°-35°.**

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | | 15°-25° | 25°-35° | |
| 10 | 27.11 | 35.35 | 44.30 | 60.9 | 61.4 | 60.7 |
| 50 | 34.70 | 45.01 | 56.56 | 78.0 | 78.1 | 77.5 |
| 200 | 39.00 | 50.34 | ..... | 87.7 | 87.4 | ..... |
| 800 | 44.48 | 57.60 | 72.95 | 100.0 | 100.0 | 100.0 |
| 1600 | 41.83 | 53.96 | 68.70 | ..... | ..... | ..... |

K 1.30 x $10^{-5}$ 1.65 x $10^{-5}$ 2.03 x $10^{-5}$.

## TABLE XXIV.

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 10 | 0.0304 | 0.0253 | 0.825 | 0.895 |
| 50 | 0.0297 | 0.0257 | 1.031 | 1.155 |
| 200 | 0.0291 | ..... | 1.134 | ..... |
| 800 | 0.0295 | 0.0266 | 1.312 | 1.535 |
| 1600 | 0.0290 | 0.0273 | 1.213 | 1.474 |

## TABLE XXV.

### Molecular Conductivity and Dissociation of Barium Chloride at 15°-25°-35°.

| | Molecular Conductivity. | | | Dissociation. | | |
|---|---|---|---|---|---|---|
| V. | 15° | 25° | 35° | 15° | 25° | 35° |
| 10 | 30.58 | 40.00 | 50.12 | 70.3 | 71.6 | 70.1 |
| 50 | 38.06 | 49.43 | 61.90 | 87.5 | 88.5 | 86.6 |
| 200 | 40.38 | 52.48 | 65.93 | 92.9 | 93.9 | 92.2 |
| 800 | 43.45 | 55.82 | 70.38 | 99.9 | 99.9 | 98.5 |
| 1600 | 43.48 | 55.86 | 71.48 | 100.0 | 100.0 | 100.0 |

K $1.58 \times 10^{-5}$ $2.02 \times 10^{-5}$ $2.45 \times 10^{-5}$.

## TABLE XXVI

### Temperature Coefficients.

| | Per cent. | | Cond. Units. | |
|---|---|---|---|---|
| V. | 15°-25° | 25°-35° | 15°-25° | 25°-35° |
| 10 | 0.0308 | 0.0253 | 0.942 | 1.012 |
| 50 | 0.0299 | 0.0234 | 1.137 | 1.157 |
| 200 | 0.0300 | 0.0256 | 1.210 | 1.345 |
| 800 | 0.0285 | 0.0261 | 1.237 | 1.456 |
| 1600 | 0.0285 | 0.0280 | 1.238 | 1.562 |

## TABLE XXVII.

**Viscosity of Solvent and Solutions at 25°.**

The last column gives the percentage increase in viscosity between the solvent and the most concentrated solution.

| Electrolyte | V = 2 | V = 4 | V = 10 | Solvent | Per Ct. Inc. |
|---|---|---|---|---|---|
| KI | 0.03710 | 0.03525 | 0.03353 | 0.03302 | 12.4 |
| NaI | 0.03997 | 0.03640 | 0.03381 | 0.03302 | 21.0 |
| $LiNO_3$ | 0.03873 | 0.03571 | 0.03157 | 0.03196 | 21.2 |
| $RbNO_3$ | 0.03430 | 0.03346 | 0.03256 | 0.03256 | 5.3 |
| RbI | 0.03615 | 0.03503 | 0.03348 | 0.03207 | 12.7 |
| CsCl | ..... | 0.03578 | 0.03395 | 0.03245 | 10.3 |
| $CsNO_3$ | ..... | 0.03478 | 0.03362 | 0.03245 | 7.2 |
| KCNS | 0.03657 | 0.03473 | 0.03280 | 0.03258 | 12.2 |
| $Na_2CrO_4$ | ..... | ..... | 0.03663 | 0.03221 | 13.7 |
| $HgCl_2$ | ..... | 0.03527 | 0.03376 | 0.03221 | 9.5 |
| $Co\ Br_2$ | ..... | ..... | 0.03699 | 0.03221 | 14.8 |
| $BaCl_2$ | ..... | ..... | 0.03702 | 0.03221 | 14.9 |

# DISCUSSION OF RESULTS

Results from the conductivity and viscosity measurements will be discussed together. The latter were made by Davis and the former by the author.

Tables III to XXVI, inclusive, give the molecular conductivity, dissociation and temperature coefficients in conductivity units and percentages, for the salts studied. Determinations were made at 15°, 25° and 35°. Table XXVII gives the viscosity of N/2, N/4 and N/10 solutions and the solvent at 25°, and the percentage increase in viscosity from the solvent to the most concentrated solution used.

In this laboratory during the past fifteen years, solutions in the following pure solvents have been investigated: Water, methyl and ethyl alcohols, acetone and glycerol. Among the results of this work in pure solvents are the discovery or confirmation of many relations between the conductivity and viscosity of solutions, the dissociation of the solutes, and the dielectric constant, association factors and viscosities of the solvents.[1] Reference to Table II shows that formamid is a solvent markedly different from any other pure solvent investigated in regard to the three constants mentioned. The most important result of this investigation is that the evidence it has developed supports and confirms all the relations and conclusions that have been worked out by Jones and his co-workers, from their investigations with other pure solvents. These relations will be discussed in turn.

The Thomson[2]-Nernst[3] theory is that the forces which hold the atoms together are electrical; hence the solvent having the highest dielectric constant has the greatest dissociating power. The dissociating power of solvents is shown in two ways: first, by comparing the percentage dissociation of solutions having the same normality, and second, by comparing the dilutions in which complete dissociation is reached. Compare Table III and IV with the following:

1. These results have been tabulated and discussed in Publications of the Carnegie Institute Nos. 170-180-210.
2. Phil. Mag. 36-320 (1893).
3. Zeit. Phys. Chem. 13-531 (1894).

**Aqueas Potassium Iodide Solution at 25°.**

| V. | $M_\nu$ | $L_a$ | Temp. Per Cent. Coef., 25°-35° |
|---|---|---|---|
| 2 | 112.8 | 76.6 | 1.85 |
| 8 | 120.7 | 82.0 | 1.97 |
| 2048 | 147.2 | 100.0 | 2.04 |

Table III shows that the dissociation of the N/2 solution of potassium iodide in formamid is only 71 per cent. at 25°. From Table XXVII, we calculate that the viscosity of the N/2 solution is 12.4 per cent. greater than the solvent, while the viscosity of the N/2 solution of potassium iodide in water is known to be less than that of the solvent. From a large mass of evidence, we know that viscosity is by far the largest factor affecting conductivity in solution in which dissociation is of the same order of magnitude. The conductivity of the N/2 solution in formamid at 25° is 18.67. We can assume without appreciable error, that if the viscosity of the solvent and the N/2 solution were in the same ratio as in the case of the potassium iodide solution in water, the conductivity of the N/2 solution in formamid would be at least 12.4 per cent. larger than the figure given—18.67. Recalculating the dissociation of the potassium iodide-formamid solution on this basis, gives 79.4 per cent.; compared with 76.6 per cent. for the potassium iodide solution in water. This latter figure would be even less if corrections were made, for the fact that the viscosity of an N/2 solution in water is less than that of the solvent, which would be a legitimate correction to make for the purpose of this comparison. Comparing in this way the dissociation of these two N/2 solutions, we find, as would be expected from the Thomson-Nernst theory, that formamid has the greater dissociating power.

Complete dissociation of potassium iodide in formamid is found in the N/200 solution, while in water it is not reached till the N/2048 solution. Therefore, in both respects, formamid falls in line with the Thomson-Nernst theory. This relation is confirmed by every salt studied in this investigation for which data for comparison are available. The rubidium salts show the stronger dissociating power of formamid much more than some others that were studied.

The hypothesis of Dutoit and Aston[4] states that the greater the association factor of the solvent, the greater its dissociating powers. Table II shows the relation of formamid to other pure solvents in regard to association factors. The correction and comparisons made above, with reference to the Thomson-Nernst

4. Compt. Rend. 125-240 (1897).

theory, are equally applicable in connection with the Dutoit and Aston theory. Having these two theories in mind, it is of interest to give here the percentage dissociation of a few salts in ethyl alcohol for comparison with the data given in Tables III, VII and XVII.

**Solutions in Ethyl Alcohol at 25°.**

| Salt | V for M∞ | $\alpha$ | for | V |
|---|---|---|---|---|
| KI | 8192 | 76.7 | | 1024 |
| KCNS | 6400 | 93.8 | | 1600 |
| $LiNO_3$ | 6400 | 89.9 | | 1600 |

The above table was taken from the data of Jones and Kreider. Jones and Mahin show that complete dissociation of lithium-nitrate in acetone is not reached even when V is 100000. The significance of these figures is apparent if one has in mind the association factors and dielectric constants of formamid, ethyl alcohol and acetone, given in Table II.

Jones and Veazey's[5] explanation of the decrease in viscosity caused in the greatest degree by caesium and rubidium salts, and in a less degree by potassium, ammonium and other salts, all having very large molecular and atomic volumes, has been of special interest in this investigation. They base their conclusion on the theory of Thorpe and Roger that viscosity is due to the friction between the surfaces of the molecules. If the particles of the solute are larger than those of the solvent, the frictional surface and, consequently, the viscosity will be decreased. If the added particles are smaller than those of the solvent, the viscosity will be increased by the addition of the solute. The viscosity of all the concentrated solutions of salts having very large atomic or molecular volumes, has been less than the solvent in the case of all pure solvents, except acetone, which have previously been studied. The viscosity of formamid has, on the contrary, been increased by every salt used. The complex formamid molecule, $HCONH_2$, and its very large association factor—6.18, show that its actual molecule is larger than that of any other pure solvent used in these investigations, and the increase in viscosity by the salts named above confirms this conclusion. The following comparison strikingly illustrates this relation: a N/2 solution of rubidium iodide in glycerol decreases the viscosity of the solvent 13 per cent., while a N/2 solution of the same salt

5. Am. Chem. Journ. 37-405 (1907)

in formamid increases the viscosity of the solvent 12.7 per cent. This relation will be referred to again in discussing the results of the work with caesium nitrate and chloride.

That the percentage temperature coefficients of conductivity increase as the viscosity of the solution increases, is a relation that has been shown by all the investigations in this laboratory. These coefficients for solutions in formamid, have the order of magnitude that would be expected from the relation of their viscosities to the viscosities of the same solutions in other solvents. For example, compare the coefficients for solutions of potassium iodide in water, given in the table on page 61 with those for the same salt in formamid in Table IV.

All salts containing water of crystallization were carefully dehydrated at suitable temperatures, just before the solutions were prepared. No thermal measurements were made of the heat of solution, but in the case of sodium iodide, which crystallizes with two molecules of water, a marked rise in temperature was noted when the salt dissolved in formamid, which indicated the formation of the solvate. It is well known that solvated salts give higher temperature percentage coefficients of conductivity than non-solvated, because complexes are usually simplified by rise in temperature. In the present investigation, salts crystallizing with water have given the larger coefficients, indicating the formation of solvates analogous to the formation by the same salts in water and other solvents. To illustrate this relation, let us compare these coefficients for sodium chromate, crystallizing with ten molecules of water (Table XX) and cobalt bromide, crystallizing with two molecules of water (Table XXIV). Also compare sodium iodide, crystallizing with two molecules of water (Table VI) with potassium iodide (Table IV). The coefficients for the dilute solutions of sodium chromate are probably not reliable for this comparison, as will be explained under the discussion of this salt.

### Sodium Chromate.

Tables XIX and XX give the results for sodium chromate. They are of the usual order of magnitude, except for the N/1600 solution. At each temperature, the increase in conductivity between the N/800 and N/1600 solutions is 59 per cent., which is probably due to chemical action or decomposition, instead of an increase in ionization. Formic acid is a strong reducing agent. Formamid may be considered as formic acid in which a hydroxyl has been replaced by an amido group. Both the hydroxyl and

amido group are basic; therefore, we might expect from this relationship that formamid would be a reducing agent. The reducing action of formamid will also be discussed with the results for mercuric chloride. Sodium chromate is a strong oxidizing agent; hence, it is not surprising that there should be chemical action between these two compounds, when the chromate is in a highly ionized condition, as in a dilute solution. The percentage dissociations have not been calculated, because the conditions just referred to introduce an uncertainty regarding them.

### Mercuric Chloride.

The conductivity of aqueous solutions of mercuric chloride is too small to be measured, but in formamid, on account of its greater dissociating power, the conductivity is measureable, and increases as dilution increases in the usual way, up to the N/400 solution. The conductivity values for the N/1000, N/1600 and N/3200 solutions clearly result from some decomposition, probably of the solvent. The conductivity of barium chloride at complete dissociation is 55.86 at 25°. The large value 134.49 for the N/1000 mercuric chloride solution, shows that it is not due to dissociation. Assuming that at complete dissociation, the conductivity of mercuric chloride would be of the same order of magnitude as of barium chloride, the dissociation of the N/4 solution would be about 1.0 per cent., increasing to about 7.0 per cent. for the N/400 solution. Silver chloride is precipitated in the N/400 solution by silver nitrate. By standing in the sunlight a short time, a heavy precipitate of metallic silver is formed, showing again the reducing action of formamid.

To recover the solvent from the mercuric chloride by vacuum distillation, required several more distillations than usual. Metallic mercury was found in the receiver after the first distillation, showing again the reducing action of formamid. It is possible that the liberated chlorine formed a salt with the formamid, which was easily dissociated, since the conductivity of the first fraction of the distillate was very high, and was lowered only a small amount by successive distillations. Repeated distillation, however, gave the solvent used for the caesium solutions.

### Cobalt Bromide.

The green anhydrous cobalt bromide gives a pink solution in formamid as in water. After the determinations were made, a mixture of solutions was distilled to recover the formamid. The

mixture contained mercuric chloride and cobalt bromide. As already stated, the mercuric chloride was reduced to metallic mercury. The dry residue in the distillation flask had the brilliant blue color of anhydrous cobalt chloride, showing that the free chlorine from the mercuric chloride had replaced the bromine in the cobalt bromide.

**Caesium Nitrate and Chloride.**

For several years past, this laboratory has been unable to obtain any caesium salts for its investigations in conductivity and viscosity. Recently some caesium sulphate was obtained through the co-operation and courtesy of Prof. James Lewis Howe, of Washington and Lee University. The sulphate was converted into the nitrate and chloride, and the conductivity and viscosity of their solutions were determined. The results are recorded in Tables XIII, XIV, XV, and XVI.

A survey of the work on the salts of all the alkali metals shows that conductivity values for the caesium, rubidium and potassium salts used are approximately the same, and for sodium and lithium are less. The same relation is true of the results obtained in aqueous solutions. Dissociation percentage is of the same order of magintude for all the salts named. The conductivity results in connection with the dissociation percentage, harmonize with the ionic velocities. For caesium, rubidium and potassium the relative ionic velocities are 73.6, 73.5 and 70.6, respectively, and for sodium and lithium they are 49.2 and 39.8.

The most striking difference between these metals is shown by the atomic volume curve of Lothar Meyer[6]. This function increases by nearly regular steps from 12 for lithium, to 72 for caesium. In accordance with Jones and Veazey's theory[7] to which reference has been made, the percentage increases in the viscosity of the concentrated solutions from the viscosity of the solvent, should be the smallest for caesium salts and should increase in the following order: Caesium, rubidium, potassium, sodium and lithium. This relation comes out clearly by comparing the figures given in the last column of Table XXVII. Compare these results for caesium and rubidium salts with those of sodium and lithium. The salts of rubidium and caesium increase the viscosity of formamid much less than sodium and lithium salts. The difference in percentages of increase is not as marked as the difference in the atomic volumes of the metal ions. The effect is partially sup-

6. Lieb. Ann. Suppl. 7-354 (1870).
7. Carnegie Institute of Washington Publication No. 80—Am. Chem. Jour. 37-405 (1907).

pressed by other factors. Consider the solution of a binary salt which is 80 per cent. dissociated. Every hundred molecules of the salt gives, in solution, eighty anions, eighty cations and twenty molecules. The eighty cations are only 44.5 per cent. of the number of particles in the solution. It is only this 44.5 per cent. of cations which have the atomic volume relations referred to above. The molecular volumes do not show this relation, and the atomic volumes of the anions are unknown.

## SUMMARY OF RESULTS.

The first six of the conclusions drawn below have been developed or confirmed by the investigations in this laboratory with other pure solvents, and have been shown by this investigation to hold true for formamid.

1. The greater the dielectric constant of a solvent, the greater its dissociating power.
2. The greater the association factor of a solvent, the greater its dissociating power.
3. The formation of solvates with formamid is indicated by those salts that form hydrates.
4. Solvated salts show larger percentage temperature coefficients of conductivity than non-solvated salts.
5. The order of magnitude of percentage temperature coefficients of conductivity is approximately proportional to the viscosity of the solutions.
6. Formamid is the first of the pure solvents studied with reference to the viscosity of solutions, in which none of the salts used produce negative viscosities. A satisfactory explanation of the above fact is apparent, if the very large association factor of the solvent is considered in connection with the theory of Jones and Veazey.
7. In regard to conductivity, dissociation and effect on viscosity of solvent, caesium salts are very closely allied to rubidium salts.
8. Formamid is a reducing agent.
9. Mercuric chloride is more dissociated in formamid than in water.

# BIOGRAPHY

The author of this dissertation was born in Grafton, Massachusetts, February 21, 1868. He graduated from the Worcester High School, and in 1889, completed the course in Civil Engineering at the Worcester Polytechnic Institute and received the degree of Bachelor of Science. Later, he was employed in the engineering departments of several bridge and construction companies. During the academic year of 1912-13, he studied Chemistry at Clark College and in the fall of 1913, entered Johns Hopkins University as a graduate student in Chemistry. His subordinate subjects were Physical Chemistry and Geology. For the year 1914-15, he was appointed Laboratory Assistant to Prof. Harry C. Jones.